

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 November 2010 (11.11.2010)

(10) International Publication Number
WO 2010/129029 A2

(51) International Patent Classification:
C07C 67/04 (2006.01)

(21) International Application Number:
PCT/US2010/001275

(22) International Filing Date:
30 April 2010 (30.04.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/387,749 7 May 2009 (07.05.2009) US

(71) Applicant (for all designated States except US):
CELANESE INTERNATIONAL CORPORATION
[US/US]; 1601 West LBJ Freeway, Dallas, TX
75234-6034 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KIMMICH, Barbara, F. M.** [US/US]; 82B Anderson Hill Road, Bernardsville, NJ 07924 (US). **TOOMEY, Hannah, E.** [US/US]; 1301 Richmond Avenue, Apt J6, Houston, TX

77006 (US). **YAO, Qiang** [CN/US]; 4641 Southpark Drive, Baton Rouge, LA 70816 (US). **TORRENCE, G., Paul** [US/US]; 4206 Masters Drive, League City, TX 77573 (US). **VAN DER WAAL, Jan, Cornelius** [NL/NL]; Schuttersveld 29, NL-2611 WE Delft (NL). **SILBEROVA, Bozena, Aeijelts, Averink** [CZ/NL]; Overblaak 22, NL-3011 MH Rotterdam (NL).

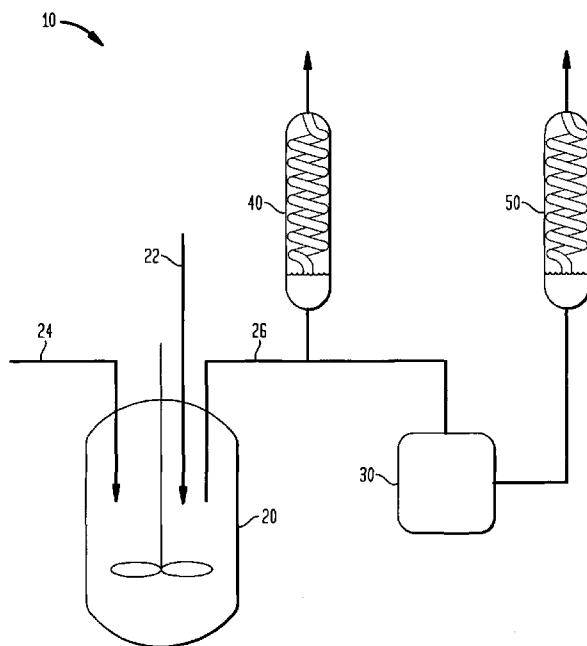
(74) Agent: **FERRELL, Michael, W.**; Ferrells, PLLC, P.O. Box 312, Clifton, VA 20124-1706 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

[Continued on next page]

(54) Title: VINYL ESTER PRODUCTION FROM ACETYLENE AND CARBOXYLIC ACID UTILIZING HETEROGENEOUS CATALYST

FIG. 1



(57) Abstract: A process for the selective production of vinyl ester by the reaction of a carboxylic acid with acetylene under heterogeneous catalytic conditions is disclosed and claimed. In a preferred embodiment of this invention, reaction of benzoic acid and acetylene in the presence of supported platinum catalyst at a temperature of from about 100 to 180°C results in quantitative yields of vinyl benzoate.

WO 2010/129029 A2

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM,

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

VINYL ESTER PRODUCTION FROM ACETYLENE AND CARBOXYLIC
ACID UTILIZING HETEROGENEOUS CATALYST

5 Claim for Priority

This non-provisional application claims the benefit of the filing date of U.S. Patent Application Serial No. 12/387,749, of the same title, filed May 7, 2009. The priority of U.S. Patent Application Serial No. 12/387,749 is hereby claimed and the disclosure thereof is incorporated into this application by
10 reference.

Field of the Invention

The present invention relates generally to a process for the production of vinyl ester from a carboxylic acid and acetylene. Specifically, the present
15 invention relates to a series of heterogeneous catalyst systems that are suitable for the production of vinyl ester from a reaction of acetylene with a variety of carboxylic acids. In the preferred embodiments, the present invention relates to formation of vinyl benzoate (VB), vinyl 2-ethyl hexanoate (V2EH), and vinyl esters of various other neo carboxylic acids using heterogeneous catalysts.
20

Background

There is a long felt need for an economically viable process for the formation of vinyl carboxylates such as, for example, vinyl benzoate. Vinyl carboxylates, such as for example vinyl benzoate, find use in a variety of
25 applications including, for example, paints, adhesives and various other coating formulations as well as cement mortar admixtures.

It is known in the art that vinyl carboxylates can be formed from the reaction of a carboxylic acid with acetylene. A variety of catalysts have been
30 proposed including base metals such as zinc, cadmium and mercury as well as precious metal catalysts such as rhenium, ruthenium, palladium, etc. In fact, the

zinc carboxylate catalyzed process has been commercialized by Hexion Specialty Chemicals for the production of VEOVA™ Monomer 10, which is a vinyl ester of VERSATIC™ Acid 10, a synthetic saturated monocarboxylic acid of highly branched structure containing ten carbon atoms. More particularly, see United States Patent No. 6,891,052 to *Tanner et al.*, wherein is disclosed a zinc carboxylate catalyst, which is used for the formation of vinyl ester from the reaction of carboxylic acid with acetylene.

Similarly, various other processes have been reported in the literature wherein a carboxylic acid is reacted with acetylene to form the corresponding vinyl ester. See United States Patent No. 3,607,915 to *Borsboom et al.* and Transition-Metal-Catalyzed Addition of Heteroatom-Hydrogen Bonds to Alkynes, *Alonso et al.*, Chem. Rev., 2004, 104 (6), 3079-3160. In particular, *Borsboom et al.* disclose generally another method involving zinc-catalyzed carboxylic acid reaction with acetylene, as already noted above. Whereas, *Alonso et al.* provide an analysis of the state of the art for catalytic addition chemistry of the reaction of acetylene with a carboxylic acid. See also, United States Patent No. 2,066,075 to *Reppe*, German Patent No. DE 740678 to *I.G. Farbenindustrie AG*, United States Patent Nos. 2,339,066 and 2,342,463 to *Fischer et al.*, British Patent No. GB 641,438A to *General Aniline and Film Corporation*, United States Patent No. 2,472,086 to *Beller et al.*, Swiss Patent No. CH 324667 to *Staeger Reinhard*, United States Patent No. 3,062,863 to *Fernholz et al.*, United States Patent No. 3,125,593 to *Hargrave et al.*, United States Patent No. 3,285,941 to *Engel et al.*, German Patent No. DE 1237557 to *Shell Internationale Research*, United States Patent No. 3,646,077 to *Hübner et al.*, and United States Patent No. 6,500,979 to *Wiese et al.*

It has also been reported in the literature that a variety of Group VIII metal complex catalysts are effective in the formation of vinyl esters by the reaction of carboxylic acids with acetylene. See, for example, United States Patent No. 3,479,392 to *Stern et al.* and United States Patent No. 5,395,960 to *Heider et al.*

Both *Stern et al.* and *Heider et al.* disclose vinylation of aromatic carboxylic acids in the presence of a catalyst based on ruthenium, rhodium, palladium, osmium, iridium, or platinum. *Stern et al.* is specifically drawn to a process for producing substituted olefins from a reactant other than acetylene or acetylenic compounds, and *Heider et al.* only disclose branched aliphatic carboxylic acids suitable for the catalyzed vinylation reaction, providing examples including 2-ethylhexanoic acid, 4-tert-butylbenzoic acid, suberic acid, and monomethyl succinate. However, *Heider et al.* disclose use of only ruthenium metal as a catalyst by way of examples and employ a very low molar ratio of carboxylic acid to ruthenium of about 25 to 100. That is, *Heider et al.* conditions require a large amount of catalyst per mole of vinyl ester produced. Additionally, *Heider et al.* employ longer reaction times of 7 to 17 hours rendering these conditions unsuitable for an industrial operation.

Palladium used as a co-catalyst with a cadmium or zinc catalyst is also known in the vinylation art. See, for example, German Patent No. DE 1161878 to *Farbwerke Hoechst Aktiengesellschaft* and British Patent No. GB 1,130,245 to *Shell Internationale Research*. Both patents disclose vinylation of benzoic acid and acetylene in the presence of a zinc or cadmium catalyst and a palladium co-catalyst. The palladium compounds taught are, however, free palladium metal or palladium chloride, and the processes are typically operated at temperatures above 120°C.

United States Patent No. 5,430,179 to *Lincoln et al.* describes a homogeneous process for vinyl ester synthesis, such as vinyl benzoate, by ruthenium-catalyzed addition of carboxylic acids, including benzoic acid, to alkynes, including acetylene. *Lincoln et al.* disclose reaction conditions that include an optional solvent, such as toluene or mineral oil, and a temperature range of from about 40 to about 200°C. *Lincoln et al.* further disclose use of a ruthenium catalyst selected from a group that includes ruthenium dodecacarbonyl in concentrations ranging from about 50,000 ppm to about 0.5 ppm ruthenium

based on the weight of the liquid phase reaction medium optionally in combination with a ligand such as triphenyl phosphine, tris(methoxyphenyl)-phosphine, or tris(p-fluoromethylphenyl)phosphine. However, *Lincoln et al.*, disclose only one example of forming vinyl pivalate from the reaction of pivalic acid with acetylene under the reaction conditions disclosed therein.

WO 2007/060176 A1 to *BASF Aktiengesellschaft* provides a process for preparing vinyl carboxylates by reacting a carboxylic acid with an alkyne compound in the presence of a catalyst selected from a group of metal compounds including rhenium-based compounds. *BASF* specifically discloses reacting benzoic acid and acetylene in the presence of dirheniumdecarbonyl; see Example 1. The Example teaches a molar ratio of carboxyl group to rhenium atom of 388, wherein the reaction takes place in a toluene solvent at 140°C over a reaction time of 6 hours. The reported yield is 99%.

15

However, it has now been found that none of the existing processes is suitable for the production of vinyl benzoate (VB) or vinyl 2-ethyl hexanoate (V2EH) via the vinylation reaction, particularly, under heterogeneous catalytic conditions. Moreover, the conventional zinc catalysts provided unacceptable reaction rates and yields for an industrial scale-up operation. In addition, there are no heterogeneous catalytic processes that are readily employable for an industrial scale continuous, semi-continuous or batch operation for the production of vinyl esters such as VB or V2EH. Thus it is desirable to develop economically viable catalytically active reactions to form VB or V2EH from their respective carboxylic acids under mild reaction conditions involving heterogeneous supported metal catalysts.

25

Summary of the Invention

It has now been unexpectedly found that vinyl benzoate can be made on an industrial scale from the reaction of a carboxylic acid, such as benzoic acid with acetylene with high selectivity and yield. More particularly, this invention

30

provides a heterogeneous process for the selective formation of vinyl esters from their corresponding carboxylic acids and acetylene, which comprises reacting a carboxylic acid, optionally dissolved in a suitable organic solvent, with acetylene in the presence of a supported metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives or a mixture thereof.

The catalyst employed in the process of this invention is a supported metal catalyst. Examples of supported metals that are suitable in the process of this invention include without any limitation iridium, palladium, platinum, rhenium, rhodium and ruthenium.

Any of the known catalyst supports can be employed to support the metals of the process of this invention. Representative catalyst supports include without any limitation, carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate, barium sulfate, and the like.

It has now been found that use of certain ligands and additives enhance the catalytic activity of certain catalysts of this invention, which aspect is described in detail hereinbelow. However, it should also be noted that other combinations of certain catalysts of this invention in the presence of certain ligands and additives exhibit diminished activity, which again becomes apparent from the detailed description that follows. Various ligands and additives that can bring about the vinylation reaction with a carboxylic acid and acetylene can be employed in the process of this invention.

It has also been found that by suitable selection of the catalyst and optionally the ligand(s) and additive(s) and utilizing them in suitable amounts results in at least 50 percent (%) conversion of a carboxylic acid and the selectivity to vinyl ester can be at least 50 percent (%). In addition, by suitable

practice of this invention it is possible to attain a Relative Activity of at least 80 and up to about 2000.

5 Other aspects and advantages of the present invention are described in the detailed description below and in the claims.

Brief Description of the Drawings:

The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts. In the **Figures:**

10

Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

15

Figure 2 is a process flow diagram illustrating one suitable industrial scale system for the production of vinyl ester from a carboxylic acid and acetylene according to this invention;

20

Figure 3 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

25

Figure 4 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples. Such discussion is for purposes of illustration only. Modifications to particular examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent

30

to one of skill in the art. Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a heterogeneous catalyst refers to a catalyst that is in a
5 different phase than the reactants during catalysis. In order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb and diffuse away from the surface. In contrast, as used herein a homogeneous catalyst refers to a catalyst that is present in the same phase as the reactants.

10

Mole percent (mole %) and like terms refer to mole percent unless otherwise indicated. Weight percent (wt % or %) and like terms refer to weight percent unless otherwise indicated.

15

“Conversion” refers to the fraction of reactant consumed in the reaction and is expressed as a mass percentage based on the amount of carboxylic acid in the feed. The conversion of carboxylic acid (CA) is calculated from gas chromatography (GC) data using the following equation:

20

$$\text{CA conversion (\%)} = 100 * \frac{\text{mass CA, in} - \text{mass CA, out (GC)}}{\text{mass CA, in}}$$

25

where mass CA, in = mass of carboxylic acid loaded (weighed in) into the reactor, and mass CA, out (GC) = mass of carboxylic acid after the reaction based on GC data.

30

“Selectivity” refers to the amount of vinyl ester produced relative to the carboxylic acid consumed and is expressed as a mole percent based on converted carboxylic acid. For example, if the conversion is 50 mole % and 50 mole % of the converted carboxylic acid is converted to vinyl ester, we refer to the vinyl

ester selectivity as 50%. Selectivity to vinyl ester (VE) is calculated from gas chromatography (GC) data using the following equation:

$$5 \quad \text{Selectivity to VE (\%)} = 100 * \frac{\text{mol VE, out (GC)}}{\text{mol CA, in} - \text{mol CA, out (GC)}}$$

“Yield” refers to the amount of vinyl ester produced relative to the carboxylic acid loaded into the reactor and is expressed as a mole percent based on carboxylic acid loaded into the reactor. Yield of vinyl ester (VE) is calculated from gas chromatography (GC) data using the following equation:

$$15 \quad \text{Yield of VE (\%)} = 100 * \frac{\text{mol VE, out (GC)}}{\text{mol CA, in (GC)}}$$

where mol CA, in = number of moles of carboxylic acid loaded (weighed in) into the reactor, mol CA, out (GC) = number of moles of carboxylic acid after the reaction based on GC data, and mol VE, out (GC) = number of moles of vinyl ester after the reaction based on GC data.

The catalyst activity is determined by Turnover Number (TON) using the following equation. TON refers to the average amount of desired product produced by each metal atom contained in the catalyst.

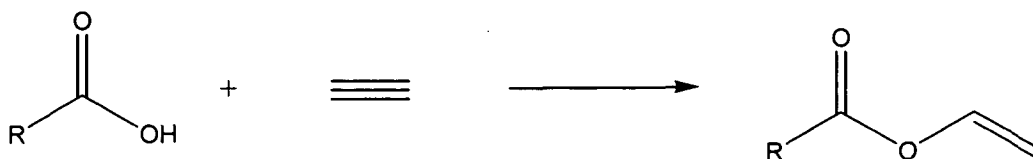
$$25 \quad \text{TON} = \frac{\text{mol VE, out (GC)}}{\text{mol Cat} * \text{N Metal atoms}}$$

30 where mol Cat = number of moles of catalysts loaded (weighed in) into the reactor, and N Metal atoms = moles of metal atoms in one mole of catalyst.

For example, a Turnover Number calculated for platinum at a 5 wt % loading on carbon used in the production of vinyl benzoate is determined by computing as the numerator: the grams of vinyl benzoate per run divided by the molecular weight of vinyl benzoate, 148.15 gm/mol; and computing as the denominator: the loading value, 0.05 times 1 gram of platinum, divided by the molecular weight of platinum, 195.084 gm/mol.

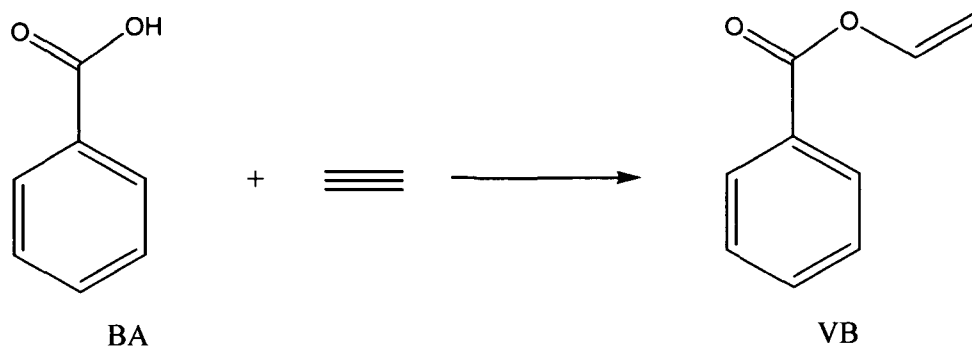
For Turnover Numbers determined under the following conditions, the Turnover Number is referred to herein as Relative Activity. The conditions for determining Relative Activity of the catalyst or system include a batch run duration of 4 hours, a charged molar ratio of carboxylic acid to catalyst metal of about 385:1, and a temperature of 120°C. When a ligand is used, the ligand is available in a molar ratio of ligand to catalyst metal of 1:1.

The reaction proceeds in accordance with the following chemical equation:

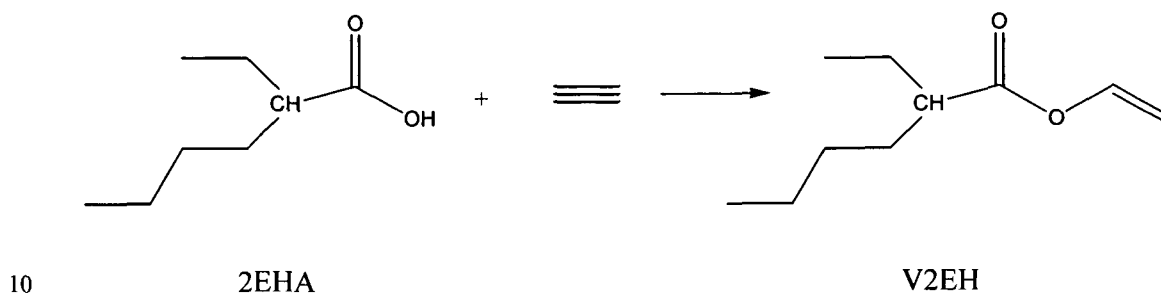


where R is an alkyl group, including a primary, a secondary or a tertiary alkyl group; a cycloalkyl group; or an aryl group such as phenyl. Thus, when R is phenyl, the acid employed is benzoic acid (BA) and the product formed is vinyl benzoate (VB) in accordance with the following chemical equation.

10



Similarly, when R is 2-ethylpentyl, the acid employed is 2-ethylhexanoic acid (2EHA) and the product formed is vinyl 2-ethylhexanoate (V2EH) in accordance with the following chemical equation.



It has now been unexpectedly found that a vinyl ester can be made on an industrial scale from the reaction of a corresponding carboxylic acid with acetylene with high selectivity and yield. More particularly, this invention provides a heterogeneous process for the selective formation of a vinyl ester from its corresponding carboxylic acid and acetylene, which comprises reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a supported metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives or a mixture thereof. Such solvents may include, for example, acetonitrile, butyl benzoate, diethyleneglycoldibutylether, mesitylene, mineral oil, and toluene.

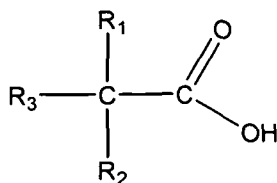
Various carboxylic acids known in the art can be employed in the process of this invention to form corresponding vinyl esters. Illustrative of suitable carboxylic acids for the practice of the invention are aliphatic or aromatic monocarboxylic, dicarboxylic and polycarboxylic acids. Examples of aliphatic monocarboxylic acids include the following: acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, 2-methylpropionic acid, 2-methylbutyric acid, 3-methylbutyric acid, 2-methylpentanoic acid, 2-ethylhexanoic acid, 2-propyl heptanoic acid; pivalic acid and other neo acids such as neodecanoic acid, neotridecanoic acid and neononanoic acid; stearic acid, and fatty acids. Examples of aromatic mono- and di-carboxylic acids include the following: benzoic acid, terephthalic acid, isophthalic acid and phthalic acid. Other aromatic carboxylic acids include substituted benzoic acid, such as for example, o-, m-, or p-toluic acid, o-, m-, or p-chlorobenzoic acid, and the like. Examples of aliphatic di- and polycarboxylic acids include: adipic acid, succinic acid, malic acid, maleic acid and polyacrylic acids. Various other carboxylic acids that are suitable in the process of this invention include crotonic acid, acrylic acid, methacrylic acid, salicylic acid, cinnamic acid, and cyclohexanoic acid.

Preferably, the acids that can be employed in the process of this invention include benzoic acid and various branched aliphatic carboxylic acids, such as for example 2-ethylhexanoic acid, 2-methylhexanoic acid, 2-ethylheptanoic acid, and the like.

Another particular class of carboxylic acids that are suitable in this invention is the neo acids. Neo acids are highly branched aliphatic carboxylic acids. In general, neo acids are trialkyl acetic acids, which include a tetra substituted alpha-carbon. Alkyl groups on the substituted alpha-carbon create a steric effect, i.e. hinder the ability of the neo acid to react. Methyl substituted alpha-carbon neo acids are the least hindered of the neo-acids. The reactivity of the neo acid primarily depends on the molecular weight and structure of the neo

acid. In general, the greater the molecular weight of the alkyl groups on the alpha-carbon, the greater the steric effect and the less reactive the neo acid. The neo acids that are suitable in this invention may be expressed according to formula I:

5



Formula I

where each of R_1 , R_2 and R_3 is an alkyl group having from 1 to 10 carbons and the total carbons in $R_1+R_2+R_3$ is from 3 to 30. Examples of neo acids include without
10 any limitation neopentanoic acid, neoheptanoic acid, neodecanoic acid, etc.

Several of the neo acids are commercially available, for example from ExxonMobil Chemical Company. Specific examples of commercially available neo acids include the ones listed above and proprietary neo acids such as neo 910 and neo 913 from ExxonMobil Chemical Company.

15

Although the process of this invention is intended to make vinyl ester from the reaction of acetylene with a carboxylic acid, various other known primary alkynes that can bring about such a vinylation reaction can also be employed in the process of this invention. Generally, unsubstituted alkynes and mono-
20 substituted alkynes that do not interfere with the addition reaction of the process of this invention may be used. Representative substituents include alkyl, alkoxy, aryl, aryloxy, acetoxy, carboxyl and halo groups. Alkynes typically have from 2 to 10 carbon atoms and suitable alkynes include substituted or unsubstituted primary alkynes such as acetylene, methyl acetylene, phenyl acetylene, 1-butyne,
25 1-pentyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and the like. More suitable alkynes useful in the practice of the invention include acetylene and methyl acetylene.

The catalyst employed in the process of this invention is a supported metal catalyst. Examples of supported metals that are suitable in this process of the invention include without any limitation iridium, palladium, platinum, rhenium, rhodium and ruthenium.

5

Any of the known catalyst supports can be employed to support the metals of the process of this invention. Representative catalyst supports include without any limitation, carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate, barium sulfate, and the like.

10

The process according to the invention may be practiced using any conventional reactor known in the art, under batch, semi-batch, or continuous conditions. The reactor may employ a fixed bed, a fluidized bed, or a moving bed. For example, a continuous stirred-tank reactor (CSTR) with acetylene sparging system, mild mechanical agitation and candle filter filtration (to hold the catalyst particles inside the reactor) can be a commercial option. Alternatively a trickle-bed, where the carboxylic acid and the acetylene are introduced co-currently from the top may be used. Another fixed bed reactor type is the bubble column where acetylene comes in from the bottom, catalyst is deposited inside the reactor tower and liquid carboxylic acid is introduced from the top. These examples are not meant to be limiting. A modern reactive distillation system where each tray is coated with catalyst can also be used, for instance.

15

20

One of skill in the art would likely select a reactor size necessary to optimize reactor throughput by whatever variable is appropriate, for instance reactor productivity (STY) or conversion. The size and shape of heterogeneous catalyst particles selected are dependent upon the type of reactor used. Thus, the catalyst may be in the form of pellets, powder, saddles, spheres, etc.

25

30

In accordance with the invention, reaction of a carboxylic acid with acetylene can be carried out in a variety of configurations such as those discussed above, including a batch reactor involving a single reaction zone and a continuous reactor wherein the reactant feed is passed through a fixed bed or a fluidized catalyst bed. The process of this invention can also be carried out using any of the other known techniques in the art such as a semi-continuous process using a stirred tank reactor, etc. For example, in a single reaction zone the catalyst may be a layered fixed bed, if so desired. An adiabatic reactor could be used, or a shell and tube reactor provided with a heat transfer medium could be used. The fixed bed can comprise a mixture of different catalyst particles which include multiple catalysts, ligands and additives as further described herein. The fixed bed may also include a layer of particulate material making up a mixing zone for the reactants. A reaction mixture including a solution of carboxylic acid, if so desired, acetylene and optionally an inert carrier gas is fed to the bed as a stream under pressure to the mixing zone. Alternatively, a carboxylic acid itself can be fed with acetylene optionally with an inert carrier gas, such as nitrogen. The stream is subsequently supplied (by way of pressure drop) to the reaction zone or layer. The reaction zone comprises a catalytic composition including a suitable supported metal catalyst where a carboxylic acid such as benzoic acid is reacted with acetylene. Any suitable particle size may be used depending upon the type of reactor, throughput requirements and so forth.

Although various metal loading levels on the supported catalysts known to one skilled in the art can be employed in the process of this invention it is preferred that a supported metal catalyst employed contains about 0.1 weight percent to about 20 weight percent of metal on a suitable catalyst support. As described further below it may also be advantageous that the supported metal catalysts that are suitable in the process of this invention may optionally contain a ligand and/or other additives including a second and/or a third supported metal on the same catalyst support. The following metals may be mentioned as those metals suitable as a second and/or third metal without any limitation: palladium,

cadmium, zinc and a mixture thereof. Typically, it is preferred that only the supported metal catalyst as described herein may be used in the process of this invention. However, other ligands and/or additives may be added to the reaction feed as additional catalytic enhancers or promoters.

5

As noted above, various catalyst supports known in the art can be used to support the catalysts of this invention. Preferred supports are carbon, activated carbon, graphite, calcium carbonate, titania, alumina, alumina-silica, and barium sulfate. More preferably, carbon, activated carbon, alumina, titania or zirconia are used as supports. It should be noted that various supported metal catalysts which are suitable in this invention are commercially available and may be used with or without catalyst activation.

In an embodiment of this invention the preferred catalyst support is carbon. Various forms of carbon known in the art that are suitable as catalyst support can be used in the process of this invention. Carbon supports that are suitable in this invention include non-activated as well as activated forms. Activation of carbon support can be performed using any of the methods known in the art. See for example, United States Patent No. 5,064,801, wherein a process for activating a certain carbon catalyst is disclosed. Another type of carbon support is a graphitized carbon, particularly the high surface area graphitized carbon as described in Great Britain Patent No. 2,136,704. The carbon is preferably in particulate form, for example, as pellets. The size of the carbon particles will depend on the pressure drop acceptable in any given reactor (which gives a minimum pellet size) and reactant diffusion constraint within the pellet (which gives a maximum pellet size).

The carbon catalyst supports that are suitable in the process of this invention preferably are porous carbon catalyst supports. With the preferred particle sizes the carbon will need to be porous to meet the preferred surface area characteristics.

30

The catalyst supports including the carbon catalyst supports may be characterized by their BET, basal plane, and edge surface areas. The BET surface area is the surface area determined by nitrogen adsorption using the method of Brunauer Emmett and Teller J. Am. Chem. Soc. 60,309 (1938). The basal plane surface area is the surface area determined from the heat of adsorption on the carbon of n-dotriacontane from n-heptane by the method described in Proc. Roy. Soc. A314 pages 473-498, with particular reference to page 489. The edge surface area is the surface area determined from the heat of adsorption on the carbon of n-butanol from n-heptane as disclosed in the Proc. Roy. Soc. article mentioned above with particular reference to page 495.

The preferred carbon catalyst supports for use in the present invention have a BET surface area of at least 100 m²/g, more preferably at least 200 m²/g, most preferably at least 300 m²/g. The BET surface area is preferably not greater than 1000 m²/g, more preferably not greater than 750 m²/g.

The preferred carbon support may be prepared by heat treating a carbon-containing starting material. The starting material may be an oleophilic graphite, e.g. prepared as disclosed in Great Britain Patent No. 1,168,785, or may be a carbon black.

As noted above, the loading levels of metal on the catalyst support is generally in the range of about 0.1 weight percent to about 20 weight percent. As already noted above, the amount of a second or third component loaded on a support is not very critical in this invention and can vary in the range of about 0.1 weight percent to about 10 weight percent. Preferably, the supported metal catalyst of this invention is free of any other loading. A metal loading of about 0.3 weight percent to about 6 weight percent based on the weight of the support is particularly preferred. Thus, for example, 0.5 to 10 weight percent of platinum supported on carbon, activated carbon, graphite, alumina, zirconia or titania is

particularly a preferred catalyst. More preferably, the platinum loading level is from about 0.5 weight percent to about 5 weight percent. Other supports suitable for supporting platinum metal include without any limitation the following: barium sulfate, calcium carbonate and silica.

5

Similarly, a catalyst containing about 1 to 3 weight percent of rhenium supported on carbon is also a preferred catalyst. Other suitable catalysts include a catalyst containing about 1 to 6 weight percent of rhodium supported on carbon, a catalyst containing about 1 to 3 weight percent of ruthenium supported on silica, 10 a catalyst containing about 1 to 6 weight percent of palladium supported on carbon, a catalyst containing about 1 to 6 weight percent of palladium supported on carbon, which may also contain about 1 to 4 weight percent of platinum as a second metal, a catalyst containing about 1 to 6 weight percent of iridium supported on carbon, a catalyst containing about 1 to 6 weight percent of iridium 15 supported on calcium carbonate and iridium (IV) oxide itself as a supported metal catalyst.

As already noted above, many of the supported metal catalysts useful in this invention are commercially available. However, the supported metal catalysts 20 can also be readily prepared using any of the methods known in the art, such as for example by metal impregnation techniques. The metal impregnation can be carried out using any of the known methods in the art. Typically, before impregnation the supports are dried at 120°C and shaped to particles having size distribution in the range of about 0.2 to 0.4 mm. Optionally, the supports may be 25 pressed, crushed and sieved to a desired size distribution. Any of the known methods to shape the support materials into desired size distribution can be employed.

For supports having low surface area, such as for example alpha-alumina, 30 the metal solutions are added in excess until complete wetness or excess liquid impregnation so as to obtain desirable metal loadings.

As noted above, the supported metal catalysts used in the process of this invention may be bimetallic catalysts. The bimetallic catalysts are generally impregnated in two steps. First, the second metal is added, followed by the “main” metal. Each impregnation step is followed by drying and calcination. The bimetallic catalysts may also be prepared by co-impregnation. In the case of trimetallic containing catalysts, a sequential impregnation may be used, starting with the addition of the secondary or tertiary metal. The second impregnation step may involve co-impregnation of the two principal metals. For example, Pd/Pt on carbon may be prepared by a first impregnation of platinum nitrate, followed by the impregnation of palladium acetate. Again, each impregnation is followed by drying and calcination. In most cases, the impregnation may be carried out using metal nitrate solutions. However, various other soluble salts which upon calcination release metal ions can also be used. Examples of other suitable metal salts for impregnation include metal hydroxide, metal oxide, metal acetate, ammonium metal oxide, such as ammonium heptamolybdate hexahydrate, metal acids, such as perrhenic acid solution, metal oxalate, and the like.

It has now been found that the use of certain ligands and additives enhance the catalytic activity of the supported metal catalysts of this invention. Various ligands and additives that can bring about the vinylation reaction with a carboxylic acid and acetylene can be employed in the process of this invention. Examples of ligands include without any limitation the following: triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, (\pm)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)ferrocene, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, diphenyl-2-pyridylphosphine, oxydi-2,1-phenylenebis(diphenylphosphine), tris(p-trifluoromethylphenyl)phosphine [P(p-CF₃C₆H₄)₃], tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine and tris(4-methoxyphenyl)phosphine.

Examples of additives include aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide,
5 sodium trifluoroacetate, potassium acetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, vinyl acetate, trirutheniumdodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine or tributylamine, tetra-(n-butyl)ammonium chloride, tetrabutylammonium acetate, sodium phosphate and tetrabutylammonium acetate.

10

In an aspect of this invention the process of this invention is generally carried out in a batch operation using a stirred tank reactor. The supported metal catalyst is slurried in a suitable solvent. To this slurry is added a solution of carboxylic acid and any desirable ligands and/or additives. The reactor is heated to
15 desirable temperatures under an inert atmosphere, such as nitrogen, and acetylene is fed into the reactor for a certain length of time. Typically, as already discussed above, the reaction times may vary depending upon the catalyst and can range from about 1 hour to 4 hours.

20

In another aspect of this invention the reaction can also be carried out in a continuous process. In this aspect, the reactants, such as benzoic acid, suitably as a solution, and acetylene, are fed into a reactor packed with the supported metal catalyst. As noted, the carboxylic acid can be fed into the reactor as a solution dissolved in a suitable solvent or neat if it is in the liquid form, such as for
25 example 2-ethylhexanoic acid. Inert gas such as nitrogen may be used as a carrier gas to feed both the carboxylic acid and acetylene at a desirable reaction temperature as discussed herein.

30

Contact or residence time can also vary widely, depending upon such variables as amount of carboxylic acid and acetylene, amount and type of catalyst and reactor, temperature and pressure employed. Typical contact times range

from a fraction of a second to more than several hours when a catalyst system other than a fixed bed is used, with preferred contact times, at least for vapor phase reactions, between about 0.5 and 100 seconds.

5 Typically, in this aspect of the invention, the catalyst employed is in a fixed bed reactor, e.g. in the shape of an elongated pipe or tube, where the reactants, typically in vapor form or as a solution, are passed over or through the catalyst. Other reactors, such as fluid or ebullient bed reactors, can be employed, if desired. In some instances, it is advantageous to use the supported metal
10 catalysts in conjunction with an inert material to regulate the pressure drop, flow, heat balance or other process parameters in the catalyst bed including the contact time of the reactant compounds with the catalyst particles.

As apparent from the Examples that follow, by practice of this invention it
15 is possible to obtain high conversion and selectivity to vinyl esters. That is, by suitable selection of the catalyst and optionally the ligand(s) and additive(s) it has now been found that high conversion of carboxylic acid to vinyl ester, for example benzoic acid to vinyl benzoate, can be achieved. More particularly, it has been
20 observed that utilization of a desirable amount of catalyst in combination with optional ligand(s) and additive(s) results in at least 50 percent (%) conversion of carboxylic acid. Additionally, the selectivity to vinyl ester is found to be at least 50 percent (%). Furthermore, by suitable practice of this invention it is possible to attain a Relative Activity of at least 80 and up to about 2000.

25 The process of this reaction can be carried out using any reaction temperature such that the intended reaction of a carboxylic acid with acetylene to form a vinyl ester can take place resulting in high selectivity to vinyl ester and at high conversions of carboxylic acid. Typically, such reactions in a batch
operation are carried out at a temperature range from about 100°C to about 180°C.
30 For example, the reaction temperature can range from about 110°C to about 170°C under certain catalytic conditions. The reaction temperature can also range from

about 120°C to about 160°C under certain other catalytic conditions. In some cases the reaction temperature ranges from about 130°C to about 150°C. In certain other situations the reaction temperature ranges from about 135°C to about 145°C. However, in a continuous operation such as the one described above even higher
5 reaction temperatures may be employed.

The reaction can also be carried out at any pressure condition so as to selectively form vinyl ester from carboxylic acid at high conversions, such as for example sub-atmospheric, atmospheric or super-atmospheric conditions.
10 Generally, it is preferred that the reaction is carried out at a pressure in the range of from about one atmosphere to two atmospheres absolute. More particularly, the reaction is carried out at atmospheric pressure conditions in an inert atmosphere, such as for example in an atmosphere of nitrogen, helium or argon.

In general, the amount of acetylenic compound employed is equimolar or slightly in excess of equimolar to the carboxylic group to be converted. Thus, when the carboxylic acid used is a mono-carboxylic acid, a molar ratio of acetylene to acid is generally from about 1:1 to 100:1, preferably from about 1.2:1 to 30:1, and more preferably from about 1.5:1 to about 10:1. Accordingly,
20 acetylenic compound is proportionately used in higher quantities when dibasic and/or other polybasic acids are employed.

In an aspect of this invention, the process of this invention can be carried out with a small amount of the catalyst. That is, large amounts of carboxylic acids
25 such as benzoic acid (BA) can be converted to a vinyl ester such as vinyl benzoate (VB) in the presence of small amounts of catalyst material. Generally, the reaction mixture comprises a mixture of desired supported metal catalyst and carboxylic acid in a molar carboxylic acid (CA) to metal ratio of from about 4000:1 to about 100:1. More typically, the molar CA/metal ratio is about 1000:1.
30 However any other molar CA/metal ratio that would bring about the desired

conversion and selectivity to vinyl ester such as VB can be employed in the process of this invention.

In another aspect of this invention, the catalyst exhibits a very high
5 Relative Activity (moles of vinyl ester/metal atom) in the process of this invention. Typically, the Relative Activities range from about 80 to about 2000, preferably Relative Activities range from about 100 to about 1500, more preferably from about 100 to about 1000.

10 In a further aspect of this invention, very high selectivity to vinyl ester, such as for example vinyl benzoate, can be obtained by suitable practice of the process of this invention. Typically, the selectivity to vinyl ester based on carboxylic acid consumed can at least be 60 percent. More specifically, the selectivity to vinyl ester based on carboxylic acid consumed may be at least 80
15 percent. Even more specifically, the selectivity to vinyl ester based on carboxylic acid consumed is at least 99 percent.

As already discussed above, depending upon the configuration of the supported metal catalyst system and the type of reactor, the process of this
20 invention can be carried out to a desirable length of time in order to obtain the best catalyst activity, Relative Activities and selectivity to vinyl ester, such as VB or V2EH. Typically, the reactions are run in a batch mode for a period ranging from about 1 hour to about 5 hours. More typically, the reaction is carried out in the batch mode for a period of about four hours. However, the process of this
25 invention can be carried out in a semi-continuous or continuous manner using any of the known process techniques in the art.

Thus in one embodiment of this invention, there is provided a supported metal catalyst wherein the metal is platinum and the catalyst support is carbon,
30 activated carbon, graphite, titania, alumina, zirconia, alumina-silica, barium sulfate and calcium carbonate. In this aspect of the invention, the loading of

platinum is from about 0.5 weight percent to about 10 weight percent, preferably from about 0.5 weight percent to about 6 weight percent. In this aspect of the invention it has now been found that the use of certain ligands as described herein may enhance the catalytic activity of the platinum as observed by increase in
5 either selectivity to vinyl ester, such as VB or conversion of carboxylic acid, such as BA or both. It has been observed that ligands such as 1,2-DPPB or triphenylphosphine generally exhibit positive or negative effects on the catalytic activity of platinum depending upon the temperature of the reaction as further discussed below. Similarly, it has also been observed that addition of certain
10 additives may also have positive effect on supported platinum catalysts. Examples of such additives include sodium benzoate, benzoic anhydride, tetrabutylammonium acetate, tributylamine, and the like. In general, the additives increase the rate of conversion of carboxylic acid, such as BA.

15 In general, it has now been found that alumina, carbon, activated carbon, zirconia and titania are the preferred catalyst supports for platinum. The following supported platinum catalysts are particularly preferred:

20 0.5% platinum supported on carbon;
1% platinum supported on carbon;
3% platinum supported on activated carbon;
5% platinum supported on activated carbon;
0.5% platinum supported on alumina;
5% platinum supported on alumina;
25 0.9% platinum supported on zirconia; and
5% platinum supported on titania.

All of the above listed supported platinum catalysts are commercially available and/or can be prepared in accordance with any of the literature
30 procedures known to one skilled in the art.

Typically, the activity of the supported platinum metal catalyst increases with increasing temperature from about 120°C to about 170°C. The Relative Activities typically increase with increasing temperature and maximum Relative Activities are typically observed at around 160°C under batch mode operation.

5 However, even higher Relative Activities may be observed in a continuous operation using a fixed bed reactor at even higher temperatures. As already noted above, use of certain ligands may have a positive or negative effect on the conversion or the selectivity especially at varied reaction temperatures. It has now been observed that the use of ligands such as triphenylphosphine or 1,2-DPPB

10 exhibit different effects on the supported platinum catalyst with varied reaction temperatures. Although both ligands generally lowered activities for supported platinum metal catalysts, Relative Activity and conversion values increase with increasing temperature in the presence of triphenylphosphine, whereas the values are evenly suppressed across temperatures in the presence of 1,2-DPPB.

15

For most supported platinum catalysts, increasing temperature generally results in an increase in the conversion of carboxylic acid, such as benzoic acid, and a decrease in the selectivity to vinyl ester, such as vinyl benzoate. However, as noted above, the temperature of about 160°C is preferred to obtain optimal

20 conversion and selectivity to vinyl benzoate in a batch mode.

25

Typically, the reaction time used in supported platinum catalysts is from about one hour to about four hours. Preferably, the reaction time is about two to about four hours.

In general, the Relative Activities increase with higher molar carboxylic acid (CA)/metal ratio. For example, the molar CA/metal ratio can range from about 300 to 4000, more preferably from about 380 to about 3000, and even more preferably from about 1200 to about 2500. Relative Activities of up to 600 or

30 higher can be achieved with 0.5% platinum supported on alumina, 0.9% platinum supported on zirconia, or 0.5% to 1% platinum supported on carbon. More

particularly, it has now been observed that at a molar BA to platinum atom ratio of about 1450, Relative Activities of about 700 can be achieved and at a molar BA to platinum atom ratio of about 2300, Relative Activities of about 700 to 800 can be achieved.

5

Generally, the type of catalyst support employed has an effect on the conversion and selectivity to vinyl ester. It has now been observed that carbon, zirconia or titania exhibit higher Relative Activities. Titania exhibits highest conversion whereas carbon exhibits highest selectivity.

10

In general, the supported platinum catalysts are dried in nitrogen atmosphere at 100°C for 16 hours before use. The tested catalysts may be reused after drying again at 100°C for 16 hours. The catalysts may also be dried at a temperature range of 50°C to 100°C in air for a sufficient length of time, such as for example about 16 hours. However, it is preferred that the supported platinum catalysts are dried in an inert atmosphere such as nitrogen.

In another embodiment of this invention, there is further provided a supported metal catalyst wherein the metal is rhenium and the catalyst support is carbon. In this aspect of the invention, the loading of rhenium is from one (1) weight percent to about six (6) weight percent, preferably the loading of rhenium is from about two (2) weight percent to about four (4) weight percent. Again in this aspect of the invention, certain of the ligands and/or additives can be used in combination with a supported rhenium catalyst. A specific example of a supported rhenium catalyst is two (2) weight percent rhenium on carbon, which is commercially available.

In another embodiment of this invention, there is further provided a supported metal catalyst wherein the metal is rhodium and the catalyst support is carbon. In this aspect of the invention, the loading of rhodium is from one (1) weight percent to about ten (10) weight percent, preferably from about two (2)

30

weight percent to about six (6) weight percent. Again in this aspect of the invention, certain ligands and/or additives can be used in combination with a supported rhodium catalyst. A specific example of a supported rhodium catalyst is five (5) weight percent rhodium on carbon, which is commercially available.

5

It has now been observed that use of triphenylphosphine with 5 weight percent rhodium on carbon has a positive effect on the conversion and selectivity to vinyl esters such as VB.

10 In another embodiment of this invention, there is further provided a supported metal catalyst wherein the metal is ruthenium and the catalyst support is silica. In this aspect of the invention, the loading of ruthenium is from one (1) weight percent to about ten (10) weight percent, preferably from about two (2) weight percent to about six (6) weight percent. Again in this aspect of the
15 invention, certain ligands and/or additives can be used in combination with a supported ruthenium catalyst. A specific example of a supported ruthenium catalyst is 1.85 weight percent ruthenium on silica, which is commercially available.

20 It has now been observed that use of a ligand such as triphenylphosphine has a positive effect on the activity of the ruthenium supported on silica. The reaction temperature that can be employed with a supported ruthenium catalyst is generally from about 150°C to about 170°C in a batch operation for the conversion of carboxylic acid to vinyl ester, such as BA to VB. Any of the solvents as
25 described herein can be employed with ruthenium catalysts, if so desired. An example of a suitable solvent is butyl benzoate.

In another embodiment of this invention, there is further provided a supported metal catalyst wherein the metal is palladium and the catalyst support is
30 carbon. This catalyst further contains a second metal which is platinum. In this aspect of the invention, the loading of palladium is from one (1) weight percent to

about ten (10) weight percent, preferably from about one (2) weight percent to about six (6) weight percent. Again in this aspect of the invention, certain ligands and/or additives can be used in combination with a supported palladium catalyst. A specific example of a supported palladium catalyst is three (3) weight percent
5 palladium on carbon, which further contains platinum. This catalyst is commercially available.

The reaction temperature that can be employed with a supported palladium catalyst is generally from about 150°C to about 170°C in a batch operation for the
10 conversion of carboxylic acid to vinyl ester, such as for example BA to VB. Again, any of the solvents as described herein can be employed with palladium catalysts, if so desired. An example of a suitable solvent is butyl benzoate.

In another embodiment of this invention, there is further provided a
15 supported metal catalyst wherein the metal is iridium and the catalyst support is either carbon or calcium carbonate. In this aspect of the invention, the loading of iridium is from one (1) weight percent to about ten (10) weight percent, preferably from about one (2) weight percent to about six (6) weight percent. Again in this aspect of the invention, certain ligands and/or additives can be used in
20 combination with a supported iridium catalyst. Specific examples of supported iridium catalysts are: five (5) weight percent iridium on carbon or five (5) weight percent iridium on calcium carbonate, both of which are commercially available. In addition, iridium(IV) oxide can be used as such in the process of this invention as a heterogeneous supported iridium metal catalyst.

25

Figure 1 illustrates a laboratory scale system **10** for the production of vinyl esters by the reaction of a carboxylic acid and acetylene using the catalyst system of this invention. The system **10** of **Figure 1** comprises a stirred reactor **20** and a collector **30**. The reactor **20** and the collector **30** are each provided with a
30 condenser **40, 50** for which a conventional means of pressure regulation is provided, such as a bubbler, not shown. Briefly, a suitable reactor **20** of desired

size, such as a 250 mL three-neck glass flask, is employed. The reactor **20** is initially charged with a desired carboxylic acid, suitable solvent and predetermined amounts of catalyst, and if necessary, ligands and additives. Then the reactor **20** is purged with nitrogen and heated to desired reaction temperature.

5 Acetylene is then bubbled into the reaction mixture at a desired rate via line **24** and additional carboxylic acid may be charged, with solvent as necessary, via line **22**. As the reaction proceeds, the vinyl ester product is removed via line **26** and is fractionated and collected in a collection flask **30**. The condensers **40**, **50** serve to recover an optimal amount of product and solvent while releasing non-

10 condensible gases. The temperature of the condensers **40**, **50** is regulated by conventional means known to one of skill in the art. The order of addition of the reactants is not crucial in the process of this invention.

Figure 2 illustrates one of a variety of suitable scaled-up reactor systems

15 **100** for industrial operation. The system **100** of **Figure 2** comprises a reactor **110**, a collection tank **120**, and a series of knock out pots represented here by a single pot **130**. The reactor **110** is charged with catalyst through the bottom of the reactor **110** and with carboxylic acid and optionally solvent via line **114**. Acetylene is bubbled through the reaction medium via line **116** under a nitrogen atmosphere.

20 The reactor is heated to a predetermined temperature and the temperature is maintained throughout a reaction time. Vinyl ester product is removed from the reactor via line **118** and collected in product collection tank **120**. Gaseous substances from the reactor **110** and the collection tank **120** are routed to knock out pot **130** via line **24**. The knock out pot(s) **130** serve to condense product and

25 solvent vapors, regulate pressure, and dilute non-condensable gases.

Examples

The following examples are presented to further illustrate the present invention and should not be taken as limiting the invention, the spirit and scope of

30 which is set forth in the appended claims. These examples are provided for

illustrative purposes only and various modifications thereof can readily be made which are known to one skilled in the art.

Examples 1-12 illustrate the conversion of benzoic acid to vinyl benzoate.
5 The selectivity to vinyl benzoate and TONs achieved by Examples 1 and 3-12 are displayed in summary form in **Figures 3 and 4**, respectively. Specifically, Example 1 illustrates the process of this invention using a supported platinum metal catalyst in a batch mode.

10 Example 2 illustrates the process of this invention using a supported platinum catalyst in a continuous operation.

Examples 3-8 illustrate the catalytic activity of various supported platinum catalysts with or without ligands and/or additives.

15 Example 9 illustrates the catalytic activity of various supported rhenium metal catalysts with or without ligands and/or additives.

Example 10 illustrates the catalytic activity of various supported rhodium
20 metal catalysts with or without ligands and/or additives.

Examples 11-12 illustrate the catalytic activity of various supported iridium metal catalysts with or without ligands and/or additives.

25 Examples 13-16 illustrate scale-up procedure for the conversion of benzoic acid to vinyl benzoate. Examples 17-18 illustrate the conversion of 2-ethyl hexanoic acid to vinyl 2-ethylhexanoate.

30 Finally, Comparative Example 1 illustrates the catalytic activity of various other supported metal catalysts for the production of vinyl benzoate under comparative reaction conditions.

As noted above, most of the supported metal catalysts are commercially available and can be used as such. The catalyst may be activated by drying in a nitrogen atmosphere at around 50-100°C for about 16 hours. The following
5 example describes a procedure for the preparation of various metal support catalysts employed in the process of this invention for illustrative purpose only.

Example A

Preparation of 1 weight percent platinum on Carbon

10 Powdered and meshed carbon (99 g) of uniform particle size distribution of about 0.2 mm is dried at 120°C in an oven under nitrogen atmosphere overnight and then cooled to room temperature. To this is added a solution of platinum nitrate (Chempur®) (1.64 g) in distilled water (16 ml). The resulting slurry is dried in an oven gradually heated to 110°C (>2 hours, 10°C/min.). The
15 impregnated catalyst mixture is then calcined at 500°C (6 hours, 1°C/min). The impregnated catalyst is finally dried in an oven at 100°C in an inert atmosphere of nitrogen for 16 hours.

Table 1 summarizes various supported metal catalysts and ligands that can
20 be used in the process of this invention to produce vinyl benzoate (VB) selectively as described herein. Also listed are the selectivity to VB and TONs that can be attained using these catalyst systems. The Examples that follow provide more detailed results. It should be noted that similar selectivity and TONs are achieved
25 for other vinyl esters such as vinyl 2-ethylhexanoate (V2EH) and/or vinyl neocarboxylates.

Table 1. Catalyst screening results within noble metal group

Metal	Supported Metal loading level/Catalyst Support/ Ligand	VB Selectivity (%)	TON
Ru	1.85% Ruthenium/Silica/PPh ₃	30	50
Rh	5% Rhodium/Carbon/PPh ₃	65	80
Pd	4% Palladium/Platinum/Carbon	20 - 60	15 - 25
	3% Palladium/Platinum/Carbon		
Re	2% Rhenium/Carbon	10	<1
Ir	5% Iridium/Calcium Carbonate	10 - 50	75-80
	5% Iridium/Carbon		
Pt	0.5% Platinum/Carbon	50-75	35-300
	1% Platinum/Carbon		
	3% Platinum/Carbon		
	0.5% Platinum/Alumina		
	0.9% Platinum/Zirconia		
	5% Platinum/Titania		

5 Gas Chromatographic (GC) Analysis of the Products

The following procedure illustrates specific GC method that can be used for the conversion of benzoic acid (BA) to vinyl benzoate (VB). Similar methods can be readily set-up for other vinyl esters.

- 10 The analysis of the products was carried out by GC using a DB-FFAP 0.25 micron column (30 m x 0.25 mm). A backflush column CP-Sil 5 (1m x 0.25 mm) was installed to prevent high boiling solvents being analyzed on the main column. The GC samples were generally prepared as follows. A final reaction mixture containing the reactant and product(s) (~1 mL) was diluted with toluene (4 mL)
- 15 containing a precise quantity of dodecane (the internal standard). The total mixture was stirred for either 5 or 30 minutes at room temperature in order to dissolve the reactant and product(s). The 0.04 mL final sample was further diluted with toluene to ensure correct concentration ranges for the GC analysis. In

some cases, the reaction mixture was diluted with 5 mL of toluene and stirred at room temperature for one hour to dissolve the reactant and product(s).

The peaks of benzoic acid and vinyl benzoate were well separated from
5 other peaks. Dodecane was used as the external standard, which was well
separated from other peaks in the chromatograph. The GC was calibrated for
benzoic acid and vinyl benzoate by analyzing a set of calibration mixtures. The
GC method was sensitive enough to detect 25 ppm of benzoic acid and 5 ppm of
vinyl benzoate. The following temperature profile was used in this GC method:
10 50°C, hold time 1 minute, ramp at 20°C/min to 160°C, hold time 0 minute, ramp at
40°C/minute to 250°C, hold time 2.25 minute – the total duration of the run = 11
minutes.

Example 1

15 A suitable reactor vessel equipped with appropriate inlets and stirring
device was charged with 100 milligrams of benzoic acid and 500 ppm of para-
benzoquinone. The reactor was purged two to three times with nitrogen and a
constant flow of nitrogen was maintained. To this mixture was added 900
milligrams of butyl benzoate with stirring and the mixture was heated slightly if
20 necessary to dissolve benzoic acid. To this solution was added 50 milligrams of
5% platinum supported on titania with stirring and the entire mixture was heated
to 180°C. The platinum catalyst was dried at 50°C in air for 16 hours prior to use.
At this time acetylene was fed into the reactor at a steady stream maintaining the
pressure of acetylene at 1.7 bars. The reaction mixture was stirred for an
25 additional 4 hour period. At this time, a sample of the reaction mixture was
removed and analyzed by GC as described above. From the GC analysis it was
observed that 65 milligrams of vinyl benzoate was formed in the reaction mixture
(54 percent yield), the TON was 280.

Example 2

The catalyst utilized is 5 weight percent platinum on titania, which is commercially available. The catalyst is dried at 100°C in nitrogen for 16 hours prior to use.

5

In a tubular reactor made of stainless steel, having an internal diameter of 30 mm and capable of being raised to a controlled temperature, there are arranged 50 ml of 5 weight percent platinum on titania. The length of the catalyst bed after charging is approximately about 70 mm.

10

A feed liquid comprised essentially of a solution of 100 grams of benzoic acid in 900 grams of toluene. The reaction feed liquid is vaporized and charged to the reactor along with acetylene and nitrogen as a carrier gas with an average combined gas hourly space velocity (GHSV) of about 2500 hr⁻¹ at a temperature of about 200°C and a pressure of 22 bar. A portion of the vapor effluent is passed through a gas chromatograph for analysis of the contents of the effluents.

15

Example 3

Example 1 was substantially repeated in several runs using the following conditions. The reaction temperature was maintained at the appropriate temperature; at least one run was operated at each of the following temperatures: 120°C, 140°C, 160°C, 170°C and 180°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and weight of the catalyst was kept similar so as to result in same metal loading level in all cases based on 50 mg of 0.5% platinum. All catalysts were dried at 50°C in air for 16 hours prior to use. The observed results of TON and yield of VB are summarized in Table 2.

20

25

Table 2

Catalyst/support	Temp. (°C)	TON	Yield of VB (%)
0.5% Pt/Alumina	140	90	15
	160	260	40
	170	75	13
0.5% Pt/Carbon	120	10	3
	140	15	3
	160	25-30	4-5
	180	40-80	7-15
1% Pt/Carbon	120	33	5
	140	60-140	10-20
	160	110-205	15-40
	170	45-265	7-42
	180	230-260	38-40
3% Pt/Activated Carbon	140	85-100	14-17
	160	170-180	25-30
	170	80-140	15-22
5% Pt/Titania	120	30	5
	140	55-110	10-17
	160	175-220	30-40
	180	180-290	49-55

Example 4

- 5 Example 1 was substantially repeated in several runs using the following conditions. The reaction temperature was maintained at the appropriate temperature; at least one run was operated at each of the following temperatures: 120°C, 140°C, 160°C, 170°C and 180°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 230 milligrams in combination with 500
- 10 ppm of para-benzoquinone and the weight of the catalyst was kept similar so as to

result in the same metal loading level in all cases based on 50 mg of 0.5% platinum. All catalysts were dried at 50°C in air for 16 hours prior to use. The observed results of TON and yield to VB are summarized in Table 3.

Table 3

Catalyst/support	Temp. (°C)	Yield to VB (%)	TON
0.5% Pt/Alumina	140	18	220
	160	24-34	320-450
	170	10	130
0.5% Pt/Carbon	120	~1	10
	140	1	15
	160	~3	35
	180	6.5	90
1% Pt/Carbon	120	6.5	90
	140	3-28	50-420
	160	10-50	180-710
	170	3-4	30-140
	180	8-35	120-520
3% Pt/Activated Carbon	140	15-17	140-260
	160	15-17	210-240
	170	4-18	40-230
5% Pt/Titania	120	6.5	90
	140	8-22	120-250
	160	25-35	350-400
	180	4-35	50-520

Example 5

- 5 Example 1 was substantially repeated in several runs using the following conditions. The reaction temperature was maintained at the appropriate temperature; at least one run was operated at each of the following temperatures: 120°C, 140°C, 160°C, 170°C and 180°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 360 milligrams in combination with 500

ppm of para-benzoquinone and the weight of the catalyst was kept similar so as to result in the same metal loading level in all cases based on 50 mg of 0.5% platinum. All catalysts were dried at 50°C in air for 16 hours prior to use. The observed results of TON, conversion and selectivity to VB are summarized in

5 Table 4.

Table 4

Catalyst/support	Temp. (°C)	TON	Selectivity to VB (%)	Conv. (%)
0.5% Pt/Alumina	140	400	65	29
	170	450	50	39
1% Pt/Carbon	120	100	80	6
	140	200-400	70-80	19-28
	160	500-790	40-60	13-55
	170	120-200	20-50	18-25
3% Pt/Activated Carbon	140	100-300	75-100	5-18
	160	550	55	50
	170	15	10	8
5% Pt/Titania	120	100	95	6
	160	400-520	60	37
	180	30-150	5	35-45

10 Example 6

Example 1 was substantially repeated in several runs using the following conditions. Three different reaction temperatures were employed: 120°C, 140°C and 160°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 360 milligrams in combination with 500 ppm of para-benzoquinone and the appropriate amount of supported platinum catalyst was added so as to maintain a molar BA/metal ratio of ~385. All catalysts were dried at 100°C in nitrogen for 16 hours prior to use. Various ligands were also used with each of the supported

platinum catalysts as summarized in Table 5. Also summarized in Table 5 are TON, conversion and selectivity to VB.

Table 5

Pt loading level/Catalyst Support/Ligand	Temp. (°C)	TON	Selectivity to VB (%)	Conv. (%)
0.5% Pt/Alumina	120	22	15	45
	140	25-35	14-15	45-60
	160	20	10	62
0.5% Pt/Alumina/1,2-DPPB	120	8	4	42
	140	0	0	55
	160	10	4	58
0.5% Pt/Alumina/ triphenylphosphine	120	20	18	38
	140	10-15	6-11	40-42
	160	25	10	70
1% Pt/Carbon	120	80	60	38
	140	80	60	32
	160	52	60	22
1% Pt/Carbon/1,2-DPPB	120	26	45-55	12-14
	140	23	40	15
	160	22	40	16
1% Pt/Carbon /triphenylphosphine	120	50	65	20
	140	58	65	22
	160	85	60	35
5% Pt/Titania	120	45	80	15
	140	65	80	25
	160	88	60	40
5% Pt/Titania/1,2-DPPB	120	0	0	0
	140	0	0	0
	160	0	0	0
5% Pt/Titania/triphenylphosphine	120	10	55	5
	140	10-30	62-65	1-10
	160	30	60	12

Example 7

Example 1 was substantially repeated in several runs using the following conditions. The reaction temperature was maintained at 140°C for all runs. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 360
5 milligrams in combination with 500 ppm of para-benzoquinone. The appropriate amount of supported platinum metal catalyst was used to attain three different levels of molar BA/metal ratios of 385, 1155 and 3850. All catalysts were dried at 100°C in nitrogen for 16 hours prior to use. Various ligands were also used with
10 these varied molar BA/metal ratios. Also summarized in Table 6 are TON, conversion and selectivity to VB.

Table 6

Pt loading level/Catalyst Support/Ligand	BA/metal ratio	TON	Selectivity to VB (%)	Conv. (%)
0.5% Pt/Alumina	385	20-30	19	45-60
	1155	200	62	28
	3850	430	85	12
0.5% Pt/Alumina/1,2-DPPB	385	0	0	55
	1155	60	62	10
	3850	100	55	5
0.5% Pt/Alumina/triphenylphosphine	385	0-20	3-10	40
	1155	180	55	28
	3850	210	100	5
1% Pt/Carbon	385	70	60	33
	1155	160	100	13
	3850	380	100	8
1% Pt/Carbon/1,2-DPPB	385	30	-	-
	1155	60	-	-
	3850	100	-	-
1% Pt/Carbon/triphenylphosphine	385	60	62	23
	1155	180	85	18
	3850	250	100	5
5% Pt/Titania	385	60	75-80	25
	1155	200	98	19
	3850	200	100	5
5% Pt/Titania/1,2-DPPB	385	10	-	-
	1155	5	-	-
	3850	20	-	-
5% Pt/Titania/triphenylphosphine	385	5-30	-	-
	1155	80	-	-
	3850	70	-	-

Example 8

Example 1 was substantially repeated in several runs using the following conditions. Two different reaction temperatures were employed: 140°C and 160°C. The selected temperature was maintained throughout the reaction. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and the appropriate amount of supported platinum catalyst required to maintain a consistent metal loading level equivalent to 50 mg of 0.5% platinum on carbon. All catalysts were dried at 100°C in nitrogen for 16 hours prior to use. Various ligands and additives were also used with a few of the supported platinum catalysts as summarized in Table 7. Also summarized in Table 7 are the conversion and selectivity to VB.

Table 7

Pt loading level/Catalyst Support/Ligand or additive	Temp. (°C)	Selectivity to VB (%)	Conv. (%)
1% Pt/Carbon	140	99	14
	180	4	77
3% Pt/activated carbon	140	98	4
	160	66	68
5% Pt/titania	140	96	18
	180	62	86
1% Pt/carbon/1,2-DPPB	140	93	3
0.5% Pt/alumina	160	90	17
5% Pt/titania (mineral oil as solvent in this run)	140	90	19
1% Pt/carbon/PPh ₃	140	85	17
1% Pt/carbon/sodium benzoate	160	82	23
5% Pt/titania/benzoic anhydride	160	76	61
0.5% Pt/carbon	140	75	1.7
	160	2	68
5% Pt/activated carbon	160	62	42
5% Pt/alumina	160	60	51
5% Pt/carbon	160	59	45
10% Pt/carbon	160	58	39
5% Pt/alumina-silica powder	160	54	30
1% Pt/carbon/tetrabutylammonium acetate	160	45	37
5% Pt/Barium sulfate	160	37	13
1% Pt/carbon/tributylamine	160	36	41
1% Pt/graphite	160	26	9
5% Pt/calcium carbonate	160	21	12
0.04% Pt/pentasil(zeolite)-alumina	160	22	36
0.9% Pt/zirconia	160	64	70
5% Pt/silica	160	20	11
0.5% Pt/alumina/1,2-DPPB	140	62	9
5% Pt/titania/PPh ₃	140	63	11

Example 9

Example 1 was substantially repeated except for using the following conditions. The amount of catalyst was 50 milligrams of two weight percent rhenium supported on carbon and the reaction was run at 140 or 160°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone. The conversion of benzoic acid at 140°C was 4% and the selectivity to VB was 3%, and at 160°C the conversion of benzoic acid was 3% and the selectivity to VB was 8%. An additional run was performed at 140°C using mineral oil as a solvent. The conversion of benzoic acid was 2% and the selectivity to VB was 2%. Finally, a run was performed using rhenium(VII) sulfide at 120°C using butyl benzoate as a solvent. The conversion of benzoic acid was 8% and the selectivity to VB was less than 1%.

Example 10

Example 1 was substantially repeated in two runs except for using the following conditions. The amount of catalyst used was 50 milligrams of five weight percent rhodium supported on carbon with and without triphenylphosphine and the reaction was run at 160°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 360 mg in combination with 500 ppm of para-benzoquinone. The conversion of benzoic acid and the selectivity to VB are summarized in Table 8.

Table 8

Rh loading level/Catalyst Support/Ligand	Temp. (°C)	Selectivity to VB (%)	Conv. (%)
5% Rh/Carbon	160	33	11
5% Rh/Carbon/PPh ₃	160	18	16

Example 11

Example 1 was substantially repeated in several runs using the following conditions. In all runs the reaction temperature was maintained at 160°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 100 mg, 200 mg and 360 mg in combination with 500 ppm of para-benzoquinone. Fifty milligrams (with 100 or 200 mg of benzoic acid) or 29.44 mg (with 360 mg of benzoic acid) of five weight percent iridium metal, supported either on calcium carbonate or carbon, was used. This resulted in molar BA/metal ratio of 67, 126 and 385 respectively for 100, 200 and 360 mg benzoic acid charged into the reactor. The TON, conversion and selectivity to VB obtained in these runs are summarized in Table 9.

Table 9

Ir loading level/Catalyst Support	Amt. of BA	TON	Selectivity to VB (%)	Conv. (%)
5% Ir/Calcium carbonate	100	15 & 23	45 & 50	48 & 80
	200	37	33	90
	360	21	18	29
5% Ir/Carbon	100	9	40	35
	360	5	11	11

15

Example 12

Example 1 was substantially repeated in three runs except for using 50 milligrams of iridium supported on a catalyst support and the reaction was run at 160°C. Butyl benzoate was used as a solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone. The conversion of benzoic acid and the selectivity to VB are summarized in Table 10.

20

Table 10

Ir loading level/Catalyst Support	Temp. (°C)	Selectivity to VB (%)	Conv. (%)
5% Ir/Calcium carbonate	160	18	29
5% Ir/Carbon	160	11	12
Ir(IV) oxide	160	2	13

Example 13

5 A suitable reactor vessel of the class shown in **Figure 2** was equipped with appropriate inlets and stirring device and was charged with 50.08 grams of benzoic acid and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this mixture was added 133 grams of butyl benzoate with stirring and the mixture was heated slightly, if necessary, to dissolve benzoic acid. To this solution was added 10 1 gram of 5% platinum supported on carbon with stirring and the entire mixture was heated to 180°C. At this time acetylene was fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 4 hour period. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was 15 observed that 25.37 grams of vinyl benzoate was formed in the reaction mixture (42 percent yield). 21 grams of unreacted benzoic acid were recovered; Conversion of BA = 59%; Selectivity to VB = 71%; and the TON was 670.

20 Example 14

A suitable reactor vessel of the class shown in **Figure 2** was equipped with appropriate inlets and stirring device was charged with 18.05 grams of benzoic acid and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this 25 mixture was added 159 grams of butyl benzoate with stirring and the mixture was heated slightly, if necessary, to dissolve benzoic acid. To this solution was added

2.67 grams of 2% platinum supported on alumina with stirring and the entire mixture was heated to 200°C. At this time acetylene was fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 4 hour period. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was observed that 5.37 grams of vinyl benzoate was formed in the reaction mixture (25 percent yield). 12.93 grams of unreacted benzoic acid were recovered; Conversion of BA = 28%; Selectivity to VB = 87%; and the TON was 130.

10 Example 15

A suitable reactor vessel of the class shown in **Figure 2** was equipped with appropriate inlets and stirring device and was charged with 18.14 grams of benzoic acid and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this mixture was added 172 grams of butyl benzoate with stirring and the mixture was heated slightly, if necessary, to dissolve benzoic acid. To this solution was added 1.65 grams of 2% platinum supported on carbon with stirring and the entire mixture was heated to 180°C. At this time acetylene was fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 2 hour period. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was observed that 4.7 grams of vinyl benzoate was formed in the reaction mixture (21 percent yield). 13.6 grams of unreacted benzoic acid were recovered; Conversion of BA = 25%; Selectivity to VB = 85%; and the TON was 190.

25

Example 16

A suitable reactor vessel of the class shown in **Figure 2** was equipped with appropriate inlets and stirring device and was charged with 10.06 grams of benzoic acid and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this mixture was added 172 grams of butyl benzoate with stirring and the mixture was

30

heated slightly, if necessary, to dissolve benzoic acid. To this solution was added 1.65 grams of 2% platinum supported on carbon with stirring and the entire mixture was heated to 200°C. Acetylene was then fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 2 hours. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was observed that 13.4 grams of vinyl benzoate was formed in the reaction mixture (32 percent yield). Conversion of BA = 51%; Selectivity to VB = 92%; and the TON was 370.

10

Example 17

A suitable reactor vessel of the class shown in **Figure 1** was equipped with appropriate inlets and stirring device and was charged with 49.74 grams of 2-ethylhexanoic acid, 136.3 grams of butyl benzoate and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this mixture was added 0.99 grams of 5% platinum supported on carbon with stirring and the entire mixture heated to 180°C. Acetylene was then fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 4 hours. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was observed that 9.9 grams of vinyl 2-ethylhexanoate was formed in the reaction mixture (17 percent yield). 33 grams of unreacted 2-ethylhexanoic acid were recovered; Selectivity to V2EH = 42%; and the TON was 240.

20

Example 18

A suitable reactor vessel of the class shown in **Figure 1** was equipped with appropriate inlets and stirring device and was charged with 40.34 grams of 2-ethylhexanoic acid, 136.3 grams of butyl benzoate and 2 grams of methylhydroquinone. The reactor was purged two to three times with nitrogen and a constant flow of nitrogen was maintained. To this mixture was added 0.99

25

grams of 5% platinum supported on carbon with stirring and the entire mixture was heated to 200°C. At this time acetylene was fed into the reactor at a steady stream and at a rate of 100 mL/min. The reaction mixture was stirred for an additional 4 hour period. At this time, a sample of the reaction mixture was removed and analyzed by GC as described above. From the GC analysis it was observed that 19.4 grams of vinyl 2-ethylhexanoate was formed in the reaction mixture (41 percent yield). Conversion of 2-EHA = 33%; Selectivity to V2EH = 58%; and the TON was 450.

10 Comparative Example 1

Example 1 was substantially repeated in several runs except for using various one or more metals supported on a catalyst support. The metals tested were aluminum, bismuth, cerium, cobalt, chromium, iron, molybdenum, nickel, lead, antimony, scandium, tin, vanadium, tungsten, and zirconium as a single metal supported on carbon. Also included in this comparative study was a catalyst comprising a combination of metals of lanthanum, cerium, cobalt, and copper supported on carbon. Another catalyst tested contained a combination of yttrium, barium and copper supported on carbon. The reactions were run at a temperature range of 50°C to 180°C depending upon the type of catalysts used as follows:

20

50°C and 10 mg of: Co, Cr, Mo, Ni and W supported catalysts;

80°C and 10 mg of: Co, Cr, Mo, Ni and W supported catalysts;

120°C and 50 mg of: Co, Cr, Mo, Ni and W supported catalysts;

160°C and 50 mg of LaCeCoCu, Ni and YBaCu supported

25

catalysts;

180°C and 50 mg of: Al, Bi, Ce, Co, Cr, Fe, Mo, Ni, Pb, Sb, Sc, Sn,

V and Zr supported catalysts.

In all runs butyl benzoate was used as the solvent. In all runs the amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and 10 or 50 milligrams of the catalyst as noted above. The results

30

showed that TONs were below 0.1 for most of the catalysts in this group, and none of the TONs exceeded 20.

While the invention has been described in connection with several
5 embodiments, modifications of those embodiments within the spirit and scope of
the present invention will be readily apparent to those of skill in the art. The
invention is defined in the appended claims.

WHAT IS CLAIMED IS:

1. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a supported metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives or a mixture thereof; wherein said supported metal is selected from the group consisting of iridium, palladium, platinum, rhenium, rhodium and ruthenium; and wherein the catalyst and optionally the ligand(s) and additive(s) are selected and utilized in amounts such that selectivity to the vinyl ester is at least 50%.
5
2. The process according to Claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50% and a relative activity of at least 80.
15
3. The process according to Claim 1, wherein said carboxylic acid is selected from the group consisting of benzoic acid, 2-ethyl hexanoic acid, neopentanoic acid, neoheptanoic acid and neodecanoic acid.
- 20 4. The process according to Claim 1, wherein the catalyst support is selected from the group consisting of carbon, activated carbon, graphite, silica, titania, alumina, calcium silicate, calcium carbonate, silica-alumina, silica aluminate, zirconia, barium carbonate and barium sulfate.
- 25 5. The process according to Claim 1, wherein the supported metal catalyst is present on the catalyst support at a loading level of about 0.1 weight percent to about 20 weight percent.
- 30 6. The process according to Claim 1, wherein an initial reaction mixture comprises a mixture of said supported metal catalyst and carboxylic acid in a molar acid:metal ratio of from about 4000:1 to about 300:1.

7. The process according to Claim 1, wherein the reaction temperature ranges from about 25°C to about 250°C.
- 5 8. The process according to Claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.
9. The process according to Claim 1, wherein the solvent is selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil,
10 diethylene glycol dibutylether and toluene.
10. The process according to Claim 1, wherein said ligand is selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, (±)-
15 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine, oxydi-2,1-phenylenebis(diphenylphosphine), tris(p-trifluoromethylphenyl)phosphine [P(p-CF₃C₆H₄)₃], tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine and tris(4-methoxyphenyl)phosphine; and said additive is selected from the group
20 consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium
25 acetylacetonate, palladium chloride, trirutheniumdodecacarbonyl (Ru₃(CO)₁₂), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tert-butylammonium acetate.
- 30 11. A heterogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in

- a suitable organic solvent, with acetylene in the presence of a supported platinum metal catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives thereof; wherein the catalyst and optionally the ligand(s) and additive(s) are selected and
5 utilized in amounts such that the relative activity is at least 100.
12. The process according to Claim 11, wherein said carboxylic acid is benzoic acid.
- 10 13. The process according to Claim 11, wherein said carboxylic acid is 2-ethylhexanoic acid.
14. The process according to Claim 11, wherein the catalyst support is carbon, activated carbon, alumina or titania.
- 15 15. The process according to Claim 11, wherein the loading level of the metal is from about 0.1 weight percent to about 10 weight percent.
16. The process according to Claim 11, wherein the carboxylic acid and catalyst
20 are provided in a molar acid:metal ratio of from about 3000:1 to about 380:1.
17. The process according to Claim 11, wherein the reaction temperature ranges from about 50°C to about 180°C.
- 25 18. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a supported platinum catalyst and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the
30 group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from

about 0.5 weight % up to about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the benzoic acid is provided in a molar ratio of benzoic acid:platinum metal of about 300:1 to about 4000:1.

5

19. The process according to Claim 18, wherein the catalyst support is carbon, activated carbon, or titania.

20. The process according to Claim 18, wherein the reaction temperature ranges
10 from about 100°C to about 180°C.

21. A heterogeneous process for the selective formation of vinyl 2-ethylhexanoate from 2-ethylhexanoic acid which comprises reacting 2-ethylhexanoic acid with acetylene, optionally in a suitable organic solvent, at a suitable
15 temperature and pressure in the presence of a supported platinum catalyst, optionally in the presence of triphenylphosphine as a ligand, and optionally in the presence of an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium acetate and tributylamine, wherein the platinum loading of the catalyst is from about 0.5 weight % up to
20 about 10 weight %, the support is selected from carbon, activated carbon, titania, alumina, or zirconia, and the 2-ethylhexanoic acid is provided in a molar ratio of 2-ethylhexanoic acid:platinum metal of about 300:1 to about 4000:1.

22. The process according to Claim 21, wherein the reaction temperature ranges
25 from about 140°C to about 200°C.

23. The process according to Claim 21, wherein the support is carbon or activated carbon and wherein the platinum is present at a loading level of from about 0.5
30 weight percent to about 6 weight percent.

24. The process according to Claim 21, wherein the support is carbon and the ligand is triphenylphosphine.
25. The process according to Claim 21, wherein the supported platinum catalyst is
5 0.5 weight percent platinum supported on carbon.
26. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum supported on carbon.
- 10 27. The process according to Claim 21, wherein the supported platinum catalyst is three (3) weight percent platinum supported on carbon.
28. The process according to Claim 21, wherein the supported platinum catalyst is a combination of palladium and platinum and the support is carbon, and
15 wherein the palladium and platinum are present at a loading level of from about 1 weight percent to about 5 weight percent.
29. The process according to Claim 21, wherein the supported platinum catalyst is one (1) weight percent platinum on carbon and the reaction temperature is
20 about 160°C.
30. A heterogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a temperature in the range of about 100°C to about
25 180°C in the presence of a supported platinum catalyst chosen from 1% platinum on carbon, 3% platinum on activated carbon, 5% platinum on titania or 0.5% platinum on alumina and optionally in the presence of triphenylphosphine as a ligand, and optionally an additive selected from the group consisting of sodium benzoate, benzoic anhydride, tetrabutylammonium
30 acetate and tributylamine.

31. The process according to Claim 30, wherein the reaction temperature ranges from about 110°C to about 170°C.
32. The process according to Claim 30, wherein the reaction temperature ranges
5 from about 120°C to about 160°C.
33. The process according to Claim 30, wherein the supported metal catalyst is five (5) weight percent platinum supported on titania.
- 10 34. The process according to Claim 30, wherein the selectivity to vinyl ester based on carboxylic acid consumed is at least 60 percent.

FIG. 1

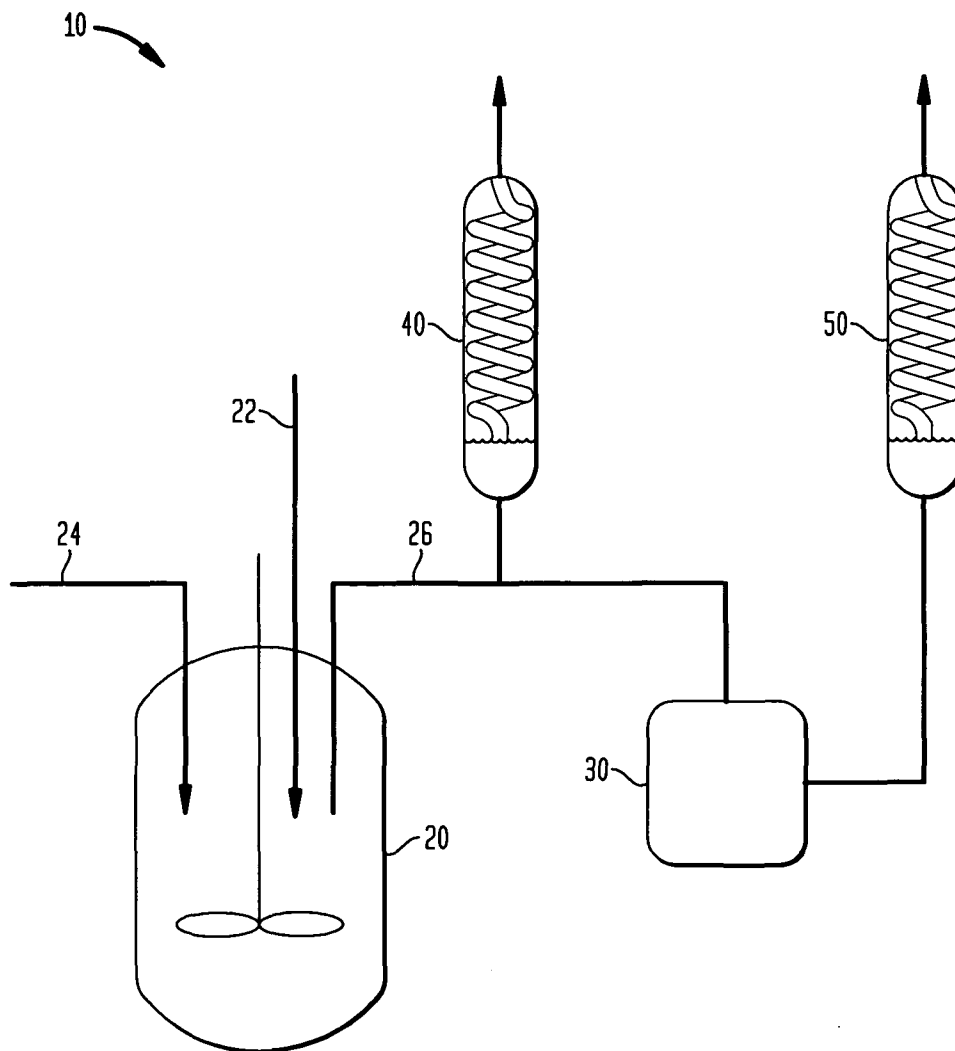
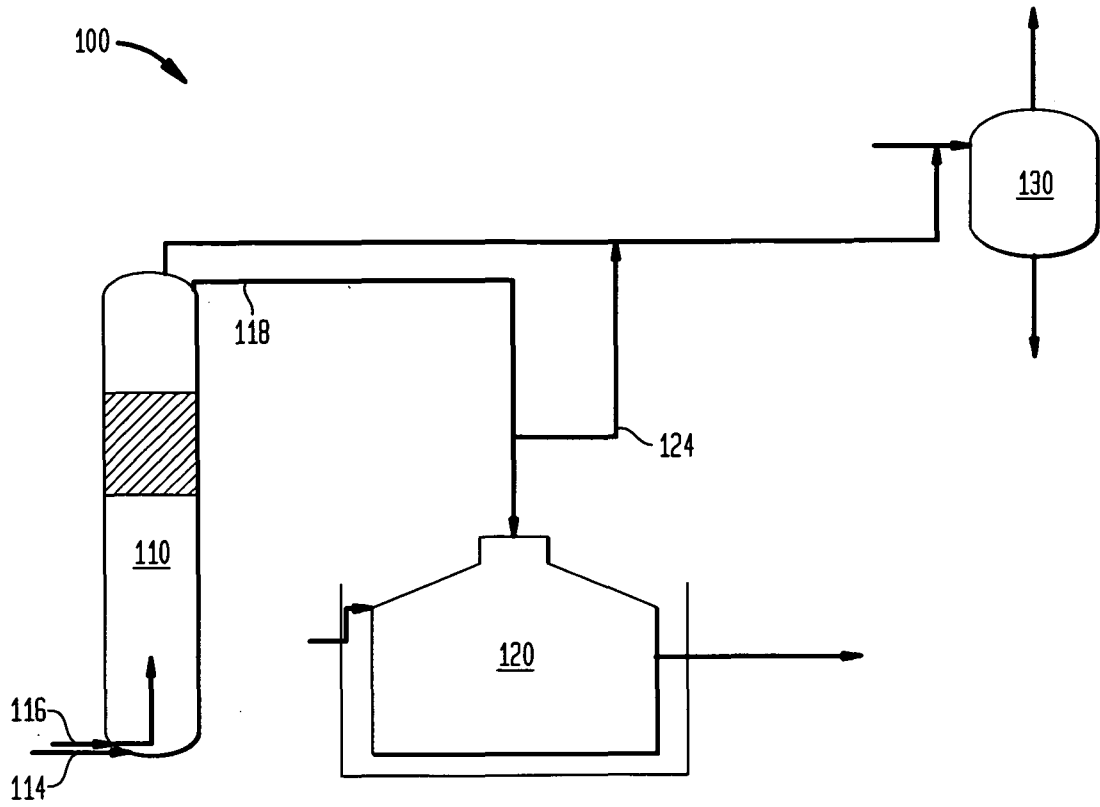


FIG. 2



3/4

FIG. 3

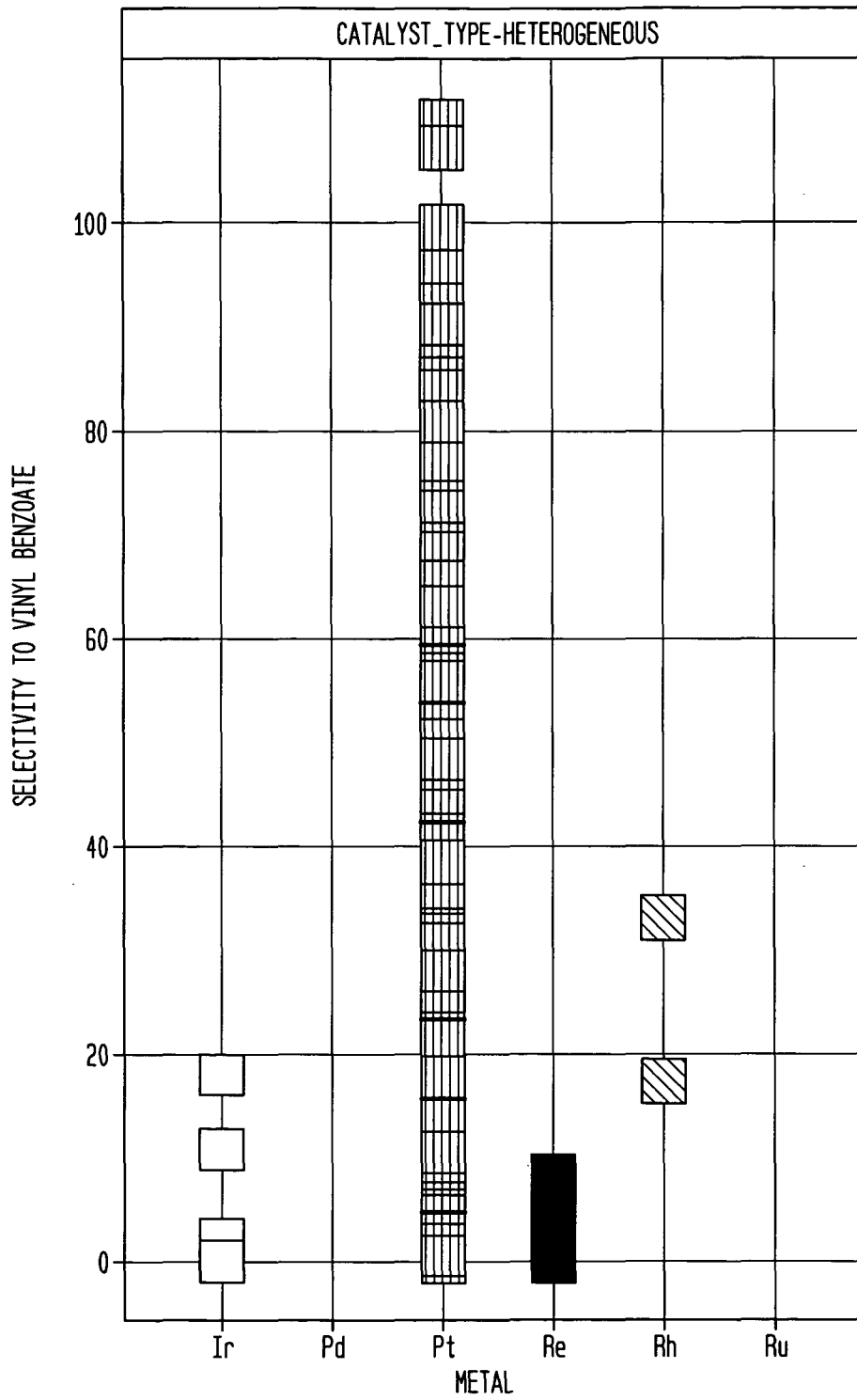


FIG. 4

