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(54) Title: PROCESS FOR MAKING POLYOL ETHERS

(57) Abstract: The present invention generally relates to a process for making polyol ethers by reacting a polyol and a carbonyl compound together in the presence of hydrogen gas and a bimetal palladium hydrogenation catalyst on a carbon support.



WO 2011/104719 A1

Process For Making Polyol Ethers

BACKGROUND OF THE INVENTION .

5 Field of the Invention.

The present invention generally relates to a process for making polyol ethers by reacting a polyol and a carbonyl compound together in the presence of hydrogen gas and a bimetal palladium hydrogenation catalyst on a carbon support.

Description of the related art.

10 Chemical and allied industries use polyol ethers such as, for example, glycerol ethers, glycol ethers and polyglycol ethers as, among other things, solvents, surfactants, wetting agents, emulsifying agents, lubricants, active ingredients in hard surface cleaning, laundry, cosmetics, personal care, ink formulations for ink-jet printing, as fabric softeners, preservatives, fragrance enhancers, and intermediates for the preparation of surfactants. They are also used in drug
15 delivery applications, treatment of allergies, and as antimicrobial agents.

A wide variety of palladium catalysts and different catalytic activities thereof are known. The variety of the palladium catalysts and their catalytic activities are a function of, among other things, the following characteristics: methods of preparing such catalysts (e.g., impregnation or incipient wetness technique, ion exchange, deposition-adsorption, deposition-precipitation, or
20 deposition-reduction); chemical composition and characteristics of the palladium starting material used in such preparation methods (e.g., H_2PdCl_4 , Na_2PdCl_4 , $Pd(NO_3)_2$, or $(NH_3)_2PdCl_6$); whether or not anions residual from the palladium starting material remain in the palladium catalyst or are removed therefrom (e.g., by washing or during activation); use of a catalyst support or not; chemical composition of the catalyst support (e.g., a support comprising silicon
25 dioxide, alumina, carbon, or zeolite); structural characteristics of the catalyst support (e.g., surface area, porosity, acidity, and particle shape); additional metal components; procedure, with respect to the palladium, by which the co-metal is added to the catalyst support (e.g., sequential to or simultaneously with the palladium); nature of the co-metal; amount of the co-metal relative to palladium; how the catalyst is activated, which in this context means how an ionic palladium
30 species is reduced to its zero-valent active metallic form (e.g., hydrogen gas acting on a dry powder form at an elevated temperature or a solution phase activation); type of reaction for which the palladium catalyst is intended; and combinations of these differences, which combinations themselves produce yet more variability (e.g., palladium catalysts prepared by different methods may have different catalytic activities and selectivities in different reactions).

35 United States (U.S.) Patent Number US 5,446,208 mentions, among other things, a process for producing ether alcohols by hydrogenolysis of cyclic ketals in the presence of a

palladium catalyst. The palladium catalyst can further comprise a co-metal such as ruthenium, rhodium, platinum, or nickel but such palladium bimetallic catalysts must have at least 50 weight percent (wt%) palladium and 50 wt% or less of the co-metal and the palladium bimetallic catalysts are of alloy-type or co-precipitated/calcined type (e.g., addition of a precipitating agent
5 such as an alkali or alkaline earth metal hydroxide or carbonate followed by calcination of resulting simultaneously precipitated palladium and co-metal salts).

US 5,446,210 mentions, among other things, a process for producing polyol ethers by reacting a mixture of at least one polyol and at least one carbonyl compound in the presence of a hydrogenation catalyst, and removing the polyol ether-containing reaction product from the
10 hydrogenation catalyst. Examples indicate the process is not selective, producing on a molar basis significantly more alcohol by-product from reduction of the carbonyl compound than the polyol ether-containing compound.

U.S. 6,265,623 B1 mentions a process for the reductive cleavage of linear and cyclic acetals, especially formals. The process is directed towards the hydrogenolytic cleavage of cyclic
15 formals in an aqueous medium in the presence of a formate salt. The process employs a hydrogenation catalyst and forms 1,3-diols and methanol.

Coq B. and Figueras, F., *Bimetallic palladium catalysts: influence of the co-metal on the catalyst performance*, Journal of Molecular Catalysis A: Chemical, 2001;173:117-134, mention, among other things, an overview about the effect of co-metal on the performance of Pd in
20 bimetallic catalysts.

Shi Y., et al., *Straightforward selective synthesis of linear 1-O-alkyl glycerol and di-glycerol monoethers*, Tetrahedron Letters, 2009;50:6891-6893, mention, among other things, a process for producing 1-O-alkyl glycerol and di-glycerol monoethers generally employing an aldehyde, glycerol or di-glycerol, hydrogen gas, and a hydrogenation catalyst of palladium on
25 carbon and a co-catalyst that is a strong Brønsted acid (i.e., having an acid dissociation constant ($\text{pK}_a \leq 2$). The process requires the co-catalyst for achieving yields of the monoethers greater than trace yields. Shi Y., et al. mention a 40:1 ratio of glycerol or di-glycerol to aldehyde is optimal.

The chemical and allied industries desire an improved hydrogenation process for making
30 polyol ethers that provides higher yields of the polyol ether, increased selectivity for making the polyol ether over by-products, or both.

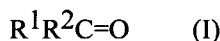
BRIEF SUMMARY OF THE INVENTION

The present invention provides a process for making polyol ethers by reacting a polyol
35 and a carbonyl compound in the presence of hydrogen gas and an improved palladium catalyst to

give higher yields of the polyol ethers and increased selectivity of the polyol ethers over by-products.

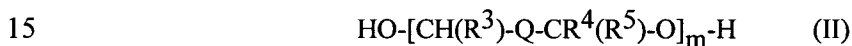
In a first embodiment the present invention is a process for making a polyol ether, the process comprising contacting together under selective hydrogenating conditions an excess
5 amount of a polyol, an amount of a carbonyl compound, an excess amount of hydrogen gas, a catalytic amount of a bimetal palladium hydrogenation catalyst, and an acidic co-catalyst so as to provide the polyol ether, wherein:

(a) the carbonyl compound is of formula (I):



10 wherein each of R^1 and R^2 independently is hydrogen atom (H), (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl-, or (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring;

(b) the polyol is a compound of formula (II):

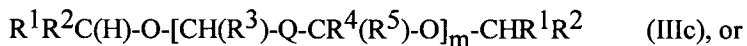
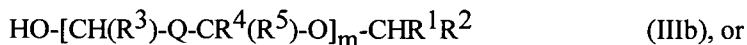
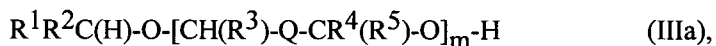


wherein m is an integer of from 1 to 2000;

each Q independently is a covalent bond (i.e., the -Q- is a covalent bond), L, X, L-X, X-L, or L-X-L, wherein each L independently is (C_1-C_{14}) alkylene, (C_1-C_{14}) heteroalkylene, or (C_2-C_{14}) alkenylene; and each X independently is
20 (C_3-C_{12}) cycloalkylene, (C_2-C_{12}) heterocycloalkylene, (C_6-C_{10}) arylene, or (C_1-C_{10}) heteroarylene;

each of R^3 , R^4 , and R^5 independently is H, (C_1-C_{20}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{10}) alkyl, or (C_3-C_{12}) cycloalkyl; or R^4 and R^5 are together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring;

25 (c) the polyol ether comprises a compound of formula (IIIa), (IIIb), or (IIIc):



a mixture of any two or more compounds of the formulas (IIIa), (IIIb), and (IIIc),

wherein R^1 and R^2 independently is hydrogen atom (H), (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a saturated (C_3-C_{12}) cycloalkyl ring; each Q independently is a covalent bond, L, X, L-X, X-L, or L-X-L, wherein each L independently is (C_1-C_{14}) alkylene or saturated (C_1-C_{14}) heteroalkylene; and each X independently is a saturated (C_3-C_{12}) cycloalkylene, saturated (C_2-C_{12}) heterocycloalkylene, (C_6-C_{10}) arylene, or (C_1-C_{10}) heteroarylene; and m and R^3 to R^5 are as defined previously; and

in (a) to (c) each alkyl, alkylene, alkenyl, alkenylene, aryl, arylene, cycloalkyl, cycloalkylene, (C_1-C_{14}) heteroalkylene, and (C_2-C_{12}) heterocycloalkylene group independently is unsubstituted or substituted with from 1 to 10 substituent groups R^S ;

each R^S is bonded to a carbon atom and independently is a hydroxyl (-OH), =O, halo, di (C_1-C_{20}) alkylamino, (C_1-C_6) alkyl, -CHO (i.e., $-C(=O)-H$), $-CO(C_1-C_6)$ alkyl (i.e., $-C(=O)-(C_1-C_6)$ alkyl), $-CO_2H$, $-CO_2(C_1-C_6)$ alkyl, $-CON((C_1-C_6)$ alkyl) $_2$, (C_1-C_6) alkoxy, (C_2-C_6) alkynyl, or -SH;

(d) the bimetal palladium hydrogenation catalyst comprises a co-adsorption of palladium and at least one co-metal that is nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium, the palladium-(co-metal) residing on a carbon support; the bimetal palladium-nickel hydrogenation catalyst being characterizable by a catalyst metal weight/weight ratio that is from less than 50 palladium:greater than 50 nickel to 20 palladium:80 nickel; the palladium hydrogenation catalyst having been prepared by independent deposition-adsorption of a palladium salt (e.g., $PdCl_2$, H_2PdCl_4 when dissolved in HCl) and a corresponding co-metal salt, respectively, on the carbon support to give at least one deposited-adsorbed material, followed by an activating reduction of the at least one deposited-adsorbed material so as to produce the bimetal palladium hydrogenation catalyst (i.e., the bimetal palladium hydrogenation catalyst is prepared by a process of the second embodiment as described later); and

(e) the process produces the polyol ether in at least 30 percent yield based on the amount of the carbonyl compound and the process is characterizable by a molar selectivity ratio of greater than 10:1 for producing the polyol ether over a potential alcohol by-product of formula (IV)

R^1R^2CHOH (IV), wherein R^1 and R^2 are as defined previously.

In a second embodiment the present invention is a process for preparing a bimetal palladium hydrogenation catalyst, the process comprising independently depositing-adsorbing a palladium salt (e.g., $PdCl_2$) and a corresponding co-metal salt that is salt of nickel, silver, iron,

chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium on a carbon support to give at least one deposited-adsorbed material; and activatingly reducing the at least one deposited-adsorbed material so as to produce a bimetal palladium hydrogenation catalyst comprising a co-adsorption of palladium and at least one co-metal that is nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium, the palladium-(co-metal) residing on the carbon support; the depositing-adsorbing steps can be performed sequentially or essentially simultaneously; and the activatingly reducing steps can be performed sequentially or essentially simultaneously (e.g., the activatingly reducing of a palladium salt-containing deposited-adsorbed material can be performed before or after depositing-adsorbing the co-metal salt and also before or after activatingly reducing a co-metal salt-containing deposited-adsorbed material).

In a third embodiment the present invention is the bimetal palladium hydrogenation catalyst prepared in the second embodiment.

As used herein, the term "acidic co-catalyst" means a Brønsted acid (i.e., protic acid) or Lewis acid characterizable as having an acid dissociation constant (pKa) less than or equal to 4 (i.e., ≤ 4).

The terms "activating reduction" and "activatingly reducing" mean adding electrons or hydrogen (e.g., via hydrogen gas or a hydride reagent such as, for example, sodium borohydride) so as to produce without calcination a functional catalyst. Without being bound by theory, the activating reduction and activatingly reducing lanthanum or cerium salts may mean subjecting such salts to such conditions, with or without reduction of lanthanum or cerium cation to lanthanum(0) or cerium(0).

The phrase "at least one deposited-adsorbed material" means a substance comprising an accumulated palladium salt, accumulated co-metal salt, or both.

The term "bimetal palladium hydrogenation catalyst" means a non-alloy substance comprising palladium(0) and at least one co-metal(0) or co-metal(cation) that is effective for increasing rate of reaction of hydrogen with a carbonyl-containing compound or an intermediate derivative thereof (e.g., an acetal or ketal derivative thereof formed *in situ*) to produce an ether-containing compound. When the co-metal is the at least one co-metal(0), the bimetal palladium hydrogenation catalyst can be referred to herein as a "bimetallic palladium hydrogenation catalyst." Preferably the co-metal(0) includes the nickel (Ni), silver (Ag), iron (Fe), chromium (Cr), molybdenum (Mo), copper (Cu), zinc (Zn), manganese (Mn), zirconium (Zr), tungsten (W), or gold (Au). A co-metal(cation) that is a La(cation) or Ce(cation) is more preferred than a co-metal(0) that is La(0) or Ce(0). Preferably the co-metal(cation) includes a cation of lanthanum (La) or cerium (Ce), respectively. A co-metal (0) that is Ni(0), Ag(0), Fe(0), Cr(0), Mo(0), Cu(0),

Zn(0), Mn(0), Zr(0), W(0), or Au(0) is more preferred than a co-metal(cation) that is a cation of Ni, Ag, Fe, Cr, Mo, Cu, Zn, Mn, Zr, W, or Au, respectively.

The term "bimetallic palladium hydrogenation catalyst" means a non-alloy substance comprising palladium(0) and at least one co-metal(0) that is effective for increasing rate of reaction of hydrogen with a carbonyl-containing compound or an intermediate derivative thereof (e.g., an acetal or ketal derivative thereof formed *in situ*) to produce an ether-containing compound.

The term "Brunauer-Emmett-Teller surface area" is described later by a procedure used to measure the surface area.

The term "carbon support" means a finely divided substance consisting essentially of a matrix of carbon atoms.

The term "catalytic amount" means a molar amount that is less than a molar amount of the carbonyl compound and at least a minimum quantity that is sufficient to facilitate production of the at least 30% yield of the polyol ether within 24 hours reaction time.

The term "co-adsorption of palladium-(co-metal)" means a non-alloy and non-precipitated substance comprising palladium and the at least one co-metal, the substance being formed by a process comprising contact and accumulation of palladium and contact and accumulation of the at least one co-metal on a surface of the carbon support, wherein such accumulations can occur essentially simultaneously, sequentially, or a combination thereof. When the palladium, at least one co-metal, or both have been accumulated as cationic precursor form(s) thereof, the accumulated precursor cationic form(s) are then chemically reduced to give accumulated palladium, accumulated at least one co-metal, or both.

The term "deposition-adsorption" means contact of a substance to and accumulation of the substance on an exposed surface of another substance (e.g., formation of metal particles followed by subsequent adsorption thereof onto a catalyst support).

The term "excess hydrogen gas" means number of moles of a gaseous substance having a molecular formula H_2 greater than number of moles of the carbonyl compound.

The term "hydrogenation" means a reaction of hydrogen with reduction in which an element (e.g., oxygen, nitrogen, sulfur, carbon, or halogen) is withdrawn from, hydrogen is added to, or the element is withdrawn from and hydrogen is added to, a molecule. Examples of hydrogenation are addition of hydrogen to a reactive molecule (e.g., addition of hydrogen to $PdCl_2$ to give Pd(0) and 2 HCl) and incorporation of hydrogen accompanied by cleavage of the molecule (i.e., hydrogenolysis, e.g., reductive cleavage of an acetal or ketal to a monoether).

The term "molar ratio" means a unitless rational or irrational number calculated by dividing number of moles of a first compound by number of moles of a second compound.

The term “percent yield” means a number of parts of the polyol ether produced per 100 parts of the carbonyl compound employed.

The term “polyol” means an organic compound having at least two hydroxyl groups, each bonded to a different carbon atom.

5 The term “selective hydrogenating conditions” mean reaction conditions such as environmental parameters and other reaction features under which a hydrogenation reaction is conducted that yields the polyol ether as described previously. The environmental parameters and other features are described in detail later.

10 The invention process advantageously produces the polyol ether in high yields (typically greater than 70% yield) and selectivities over by-products. The invention discovered the *in situ* formation of intermediate acetal or ketal from dehydrating condensation of the polyol and carbonyl compound produces the polyol ether in higher yields and selectivities than corresponding reactions employing the acetal or ketal in place of the carbonyl compound. The invention discovered that the bimetal palladium hydrogenation catalyst facilitates increased
15 catalytic activity thereof compared to other palladium catalysts that lack the co-metal feature thereof and have a same palladium composition weight percent, and even compared to bimetallic palladium catalysts that have been prepared by methods other than the instant deposition-adsorption/reduction such other methods being, for example, co-precipitation or calcination (e.g., to form alloys).

20 The higher yields of and increased selectivities for the polyol ethers makes the invention process especially valuable in the preparation of polyol ethers for use as, for example, solvents, surfactants, wetting agents, emulsifying agents, lubricants, and intermediates for the preparation of surfactants.

25 Additional embodiments are described in the remainder of the specification, including the claims.

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention provides a process for making polyol ethers by reacting a polyol and a carbonyl compound in the presence of hydrogen gas and a bimetal palladium hydrogenation catalyst to give higher yields of the polyol ethers and increased selectivity of the polyol ethers over by-products, all as summarized previously.

35 For purposes of United States patent practice and other patent practices allowing incorporation of subject matter by reference, the entire contents – unless otherwise indicated – of each U.S. patent, U.S. patent application, U.S. patent application publication, PCT international patent application and WO publication equivalent thereof, referenced in the instant Summary or Detailed Description of the Invention are hereby incorporated by reference. In an event where

there is a conflict between what is written in the present specification and what is written in a patent, patent application, or patent application publication, or a portion thereof that is incorporated by reference, what is written in the present specification controls.

5 In the present application, any lower limit of a range of numbers, or any preferred lower limit of the range, may be combined with any upper limit of the range, or any preferred upper limit of the range, to define a preferred aspect or embodiment of the range. Each range of numbers includes all numbers, both rational and irrational numbers, subsumed within that range (e.g., the range from about 1 to about 5 includes, for example, 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

10 In an event where there is a conflict between a unit value that is recited without parentheses, e.g., 2 inches, and a corresponding unit value that is parenthetically recited, e.g., (5 centimeters), the unit value recited without parentheses controls.

In the event there is a discrepancy between a chemical name and structure, the structure controls.

15 As used herein, "a," "an," "the," "at least one," and "one or more" are used interchangeably. In any aspect or embodiment of the instant invention described herein, the term "about" in a phrase referring to a numerical value may be deleted from the phrase to give another aspect or embodiment of the instant invention. In the former aspects or embodiments employing the term "about," meaning of "about" can be construed from context of its use. Preferably "about" means from 90 percent to 100 percent of the numerical value, from 100 percent to 110 percent of the numerical value, or from 90 percent to 110 percent of the numerical value. In any aspect or embodiment of the instant invention described herein, the open-ended terms "comprising," "comprises," and the like (which are synonymous with "including," "having," and "characterized by") may be replaced by the respective partially closed phrases "consisting essentially of," "consists essentially of," and the like or the respective closed phrases "consisting of," "consists of," and the like to give another aspect or embodiment of the instant invention. In the present application, when referring to a preceding list of elements (e.g., ingredients), the phrases "mixture thereof," "combination thereof," and the like mean any two or more, including all, of the listed elements. The term "or" used in a listing of members, unless stated otherwise, refers to the listed members individually as well as in any combination, and supports additional embodiments reciting any one of the individual members (e.g., in an embodiment reciting the phrase "10 percent or more," the "or" supports another embodiment reciting "10 percent" and still another embodiment reciting "more than 10 percent."). The term "optionally" means "with or without." For example, "optionally an additive" means with or without an additive. The term "plurality" means two or more, wherein each plurality is independently selected unless indicated otherwise. The symbols " $\leq$ " and " $\geq$ " respectively mean less than or equal to and greater than or equal to. The symbols "<" and ">" respectively mean less than and greater than.

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As used herein, the terms “(C₁-C₅₀)alkyl” and “(C₁-C₂₀)alkyl” mean a straight or branched, saturated hydrocarbon radical of from 1 to 50 carbon atoms or from 1 to 20 carbon atoms respectively (e.g., methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 1,1-dimethylethyl, et cetera. The alkyl groups can be unsubstituted or substituted as described previously.

5 The term “(C₂-C₅₀)alkenyl” means a straight or branched, unsaturated non-aromatic hydrocarbon radical of from 2 to 50 carbon atoms and 1, 2, or 3 carbon-carbon double bonds. The alkenyl group can be unsubstituted or substituted as described previously.

The term “(C₁-C₁₄)alkylene” means a straight or branched, saturated hydrocarbon diradical of from 1 to 14 carbon atoms. The alkylene group can be unsubstituted or substituted as described previously.

10 The term “(C₂-C₁₄)alkenylene” means a straight or branched, unsaturated non-aromatic hydrocarbon diradical of from 2 to 14 carbon atoms and 1, 2, or 3 carbon-carbon double bonds. The alkenylene group can be unsubstituted or substituted as described previously.

The term “(C₆-C₁₀)aryl” means an aromatic monocyclic or bicyclic hydrocarbon radical of from 6 to 10 ring atoms (e.g., phenyl or naphthyl). The aryl group can be unsubstituted or substituted as described previously.

The term “(C₆-C₁₀)arylene” means an aromatic monocyclic or bicyclic hydrocarbon diradical of from 6 to 10 ring atoms (e.g., phenylene or naphthylene). The arylenylene group can be unsubstituted or substituted as described previously.

20 The terms “(C₆-C₁₀)aryl-(C₁-C₅₀)alkyl” and “(C₆-C₁₀)aryl-(C₂-C₅₀)alkenyl” mean a (C₆-C₁₀)aryl substituted (C₁-C₅₀)alkyl or (C₂-C₅₀)alkenyl, wherein the (C₆-C₁₀)aryl, (C₁-C₅₀)alkyl, and (C₂-C₅₀)alkenyl are as described previously.

The term “(C₃-C₁₂)cycloalkyl” means a non-aromatic monocyclic hydrocarbon radical of from 3 to 12 ring atoms and saturated (i.e., 0 carbon-carbon double bonds) or unsaturated (i.e., 1 or 2 carbon-carbon double bonds). Examples of saturated (C₃-C₁₂)cycloalkyl are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, et cetera to cyclododecyl. Examples of unsaturated (C₃-C₁₂)cycloalkyl are cyclopropen-1-yl, cyclobuten-3-yl, and cyclopentadien-5-yl. The cycloalkyl group can be unsubstituted or substituted as described previously.

25 The term “(C₃-C₁₂)cycloalkylene” means a non-aromatic monocyclic hydrocarbon diradical of from 3 to 12 ring atoms and saturated (i.e., 0 carbon-carbon double bonds) or unsaturated (i.e., 1 or 2 carbon-carbon double bonds). Examples of saturated (C₃-C₁₂)cycloalkylene are cyclopropylene, cyclobutylene, cyclopentylene, cyclohexylene, et cetera to cyclododecylene. Examples of unsaturated (C₃-C₁₂)cycloalkylene are cyclopropen-1,3-

diyl and cyclopentadien-1,2-diyl. The cycloalkylene group can be unsubstituted or substituted as described previously.

The term “(C₁-C₁₄)heteroalkylene” means a straight or branched, non-aromatic heterohydrocarbon diradical of from 1 to 14 carbon atoms; and saturated (i.e., 0 carbon-carbon double bonds) or unsaturated (i.e., 1, 2, or 3 carbon-carbon double bonds); and 1 to 4 heteroatoms, each heteroatom independently being O, S, N, or P. Examples are CH₂CH₂O, CH₂CH₂CH₂O, CH₂CH₂CH₂CH₂O, N(H)CH₂CH₂N(H), CH₂CH₂SCH₂, and PCH₂. The heteroalkylene group can be unsubstituted or substituted as described previously.

The term “(C₂-C₁₂)heterocycloalkylene” means a non-aromatic monocyclic heterohydrocarbon diradical of from 2 to 14 carbon atoms; and saturated (i.e., 0 carbon-carbon double bonds) or unsaturated (i.e., 1, 2, or 3 carbon-carbon double bonds); and 1 to 4 heteroatoms, each heteroatom independently being O, S, N, or P. Examples are and epoxide-2-yl and tetrahydrofuran-2-yl. The heterocycloalkylene group can be unsubstituted or substituted as described previously.

The term “(C₁-C₁₀)heteroarylene” means an aromatic monocyclic or bicyclic heterohydrocarbon diradical of from 1 to 10 carbon atoms; and 1 to 4 heteroatoms, each heteroatom independently being O, S, N, or P. Examples are tetrazol-1,5-diyl and pyridine-2,5-diyl. The heteroarylene group can be unsubstituted or substituted as described previously.

In some embodiments the carbonyl compound is the compound of formula (I) wherein R¹ is H and R² is (C₁-C₅₀)alkyl, (C₂-C₅₀)alkenyl, (C₆-C₁₀)aryl-(C₁-C₅₀)alkyl, (C₆-C₁₀)aryl-(C₂-C₅₀)alkenyl-, or (C₃-C₁₂)cycloalkyl. In some embodiments each of R¹ and R² independently is (C₁-C₅₀)alkyl, (C₂-C₅₀)alkenyl, (C₆-C₁₀)aryl-(C₁-C₅₀)alkyl, (C₆-C₁₀)aryl-(C₂-C₅₀)alkenyl-, or (C₃-C₁₂)cycloalkyl. In some embodiments R¹ and R² together with the carbon atom to which they are both attached form a (C₃-C₁₂)cycloalkyl ring.

In some embodiments R¹ or R² but not both, or each of R¹ and R², independently is (C₁-C₅₀)alkyl, in other embodiments (C₂-C₅₀)alkenyl, in still other embodiments (C₆-C₁₀)aryl-(C₁-C₅₀)alkyl, in even other embodiments (C₆-C₁₀)aryl-(C₂-C₅₀)alkenyl-, and in yet other embodiments (C₃-C₁₂)cycloalkyl. Preferably R¹ and R² are not both H, i.e., the carbonyl compound is not formaldehyde.

In some embodiments the carbonyl compound is glutaraldehyde, formaldehyde, acetaldehyde, acrolein, propionaldehyde, butyraldehyde, crotonaldehyde, caproic aldehyde, caprylic aldehyde, capric aldehyde, lauryl aldehyde, myristyl aldehyde, cetyl aldehyde, stearyl

aldehyde, oleyl aldehyde, elaidyl aldehyde, linolyl aldehyde, linolenyl aldehyde, behenyl aldehyde, erucyl aldehyde, isobutyraldehyde, n-butyraldehyde, methylethylketone, 2-undecanone, *normal*-decanal (i.e., n-decanal), 2-methylundecanal, n-valeraldehyde, iso-valeraldehyde, n-hexanal, n-heptanal, 2-ethylhexanal, acetone, methylethylketone, 2-pentanone, 3-pentanone, cinnamaldehyde, levulinic acid, 1,3-cyclohexanedicarboxaldehyde, 1,4-cyclohexanedicarboxaldehyde, cyclohexanone, or a mixture of two or more thereof.

A more preferred carbonyl compound is n-butyraldehyde, methylethylketone, 2-undecanone, n-decanal, 2-methylundecanal, n-valeraldehyde, iso-valeraldehyde, n-hexanal, n-heptanal, 2-ethylhexanal, acetone, methylethylketone, 2-pentanone, 3-pentanone, cinnamaldehyde, levulinic acid, 1,3-cyclohexanedicarboxaldehyde, 1,4-cyclohexanedicarboxaldehyde, cyclohexanone, or a mixture of two or more thereof. In one particular embodiment, the carbonyl compound is a mixture of 1,3-cyclohexanedicarboxaldehyde and 1,4-cyclohexanedicarboxaldehyde. In the case of unsaturated carbonyl compounds, the double bonds thereof may be hydrogenated during the reaction to form saturated derivatives.

As mentioned previously, the invention encompasses carbonyl compounds that are unsubstituted or substituted. The substituted carbonyl compounds are capable of undergoing additional or tandem reactions to form further materials during the process of the invention. For instance, where a substituent R^S is carboxylic acid (-COOH), such as in levulinic acid, the carboxylic acid moiety is capable of undergoing esterification in tandem with the etherification of the carbonyl portion of the molecule.

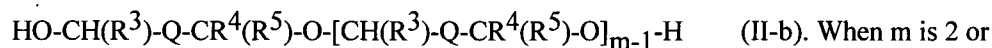
The carbonyl compounds are available from a variety of commercial sources, can be readily prepared by a person of ordinary skill in the art using well known techniques, or both. The source of the carbonyl compound and its method of preparation are not critical to the invention. For instance, aldehydes derived from seed oils or other natural sources are encompassed, as well as aldehydes that are by-products of industrial processes, or aldehydes derived from hydroformylation reactions.

In some embodiments the polyol is the compound of formula (II) wherein m is 1 and -Q- is methylene or -CH(OH)-. Preferably R^3 to R^5 each are H, i.e., the compound of formula (II) is glycerol.

In some embodiments the polyol is the compound of formula (II) wherein m is 1 and -Q- is a covalent bond, thereby giving a polyol that is compound of formula (II-a):

$HO-CH(R^3)-CR^4(R^5)-OH$ (II-a). In some embodiments R^3 and R^4 each are H and R^5 is (C_1-C_{14}) alkyl. Preferably the (C_1-C_{14}) alkyl is (C_1-C_6) alkyl. More preferably R^3 and R^4 each are H and R^5 is methyl, i.e., the compound of formula (II-a) is propylene glycol.

In other embodiments m is 2 or more, thereby giving a polyol that is compound of formula (II-b):



When m is 2 or more each Q can be the same or different. Preferably, however, each Q is the same. Preferably each Q independently is (C₁-C₁₄)alkylene or (C₁-C₁₄)heteroalkylene, more preferably each Q independently is a (C₁-C₆)alkylene, and still more preferably each Q independently is methylene (i.e., CH₂) or ethylene (CH₂CH₂). Preferably m is 500 or less, more preferably 100 or less, still more preferably 10 or less, and even more preferably 5 or less. In some embodiments m is 2, in other embodiments m is 3, in still other embodiments m is 4, in yet other embodiments m is 5, and in still yet other embodiments m is 6.

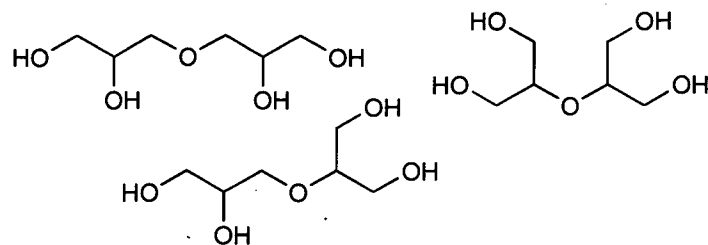
In some embodiments the polyol is a compound of formula (II) wherein each of R³ to R⁵ is H. In some embodiments two of R³ to R⁵ is H and the other one of R³ to R⁵ is (C₁-C₂₀)alkyl, (C₆-C₁₀)aryl-(C₁-C₁₀)alkyl, or (C₃-C₁₂)cycloalkyl. In some embodiments the other one of R³ to R⁵ is (C₁-C₂₀)alkyl, in other embodiments (C₆-C₁₀)aryl-(C₁-C₁₀)alkyl, and in still other embodiments (C₃-C₁₂)cycloalkyl.

In some embodiments one of R³ to R⁵ is H and the other two of R³ to R⁵ each independently is (C₁-C₂₀)alkyl, (C₆-C₁₀)aryl-(C₁-C₁₀)alkyl, or (C₃-C₁₂)cycloalkyl. In some embodiments each of the other two of R³ to R⁵ independently is (C₁-C₂₀)alkyl. In some embodiments R³ is H and R⁴ and R⁵ are together with the carbon atom to which they are both attached form a (C₃-C₁₂)cycloalkyl ring.

In some embodiments the polyol comprises a 1,2-diol moiety [i.e., C(OH)-C(OH)]. In some embodiments the polyol comprises a 1,3-diol moiety [i.e., C(OH)-C-C(OH)]. In some embodiments the polyol lacks a 1,2-diol and 1,3-diol moiety.

In some embodiments the polyol is a polyalkylene glycol, more preferably a polyethylene glycol, polypropylene glycol, or polybutylene glycol. In some embodiments the polyol is ethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; a polyethylene glycol with a number average molecular weight ranging from 62 grams per mole (g/mol) to 620 g/mol; 1,2-propylene glycol; 1,3-propylene glycol; 1,2-butylene glycol; 1,3-butylene glycol; 1,4-butylene glycol; or a mixture of any two or more thereof.

In some embodiments the polyol is glycerol; sorbitol; mannitol; 2-hydroxymethyl-1,3-propanediol; 1,1,1-tris(hydroxymethyl) ethane; trimethylolpropane; pentaerythritol; diglycerol; or a mixture of any two or more thereof. Examples of such polyols are drawn below:



Preferably the at least two hydroxyl groups of the polyol are non-phenolic or non-enolic, and more preferably both.

The polyol is available from a variety of commercial sources, can be readily prepared by a person of ordinary skill in the art using well known techniques, or both. The source of the polyol is not critical to the invention. In some embodiments, obtaining the polyol from renewable non-petroleum sources such as a biobased feedstock is desirable. Bio-based polyols are described, for instance, in U.S. Patent Application Publication numbers US 2007/0129451 A1 and US 2008/0103340 A1.

In some embodiments the polyol ether comprises the compound of formula (IIIa), in other embodiments the compound of formula (IIIb), in still other embodiments the compound of formula (IIIc), and in yet other embodiments the mixture of any two or more compounds of the formulas (IIIa), (IIIb), and (IIIc). Purity and structure or composition of the polyol ether can be readily determined using structure or composition information about the carbonyl compound and polyol and well known characterization techniques. Examples of suitable well known characterization techniques are chromatography (e.g., gas chromatography (GC)), nuclear magnetic resonance (NMR) spectroscopy (e.g., proton NMR, carbon-13 NMR, or both), mass spectrometry (MS; e.g., GC-MS), infrared spectroscopy, one or more polymer characterization techniques (e.g., dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA)), or a combination thereof.

In some embodiments the invention process forms *in situ* an acyclic acetal or ketal intermediate from the polyol and carbonyl compound. Preferably the invention process forms the acyclic acetal or ketal with a polyol lacking the aforementioned 1,2-diol and 1,3-diol moieties. In some embodiments the invention process forms *in situ* a cyclic acetal or ketal intermediate. Preferably the invention process forms the cyclic acetal or ketal with a polyol comprising the aforementioned 1,2-diol or 1,3-diol moiety. The invention contemplates recycling unreacted acetal or ketal intermediate, with or without isolation thereof from an invention reaction mixture containing the acetal or ketal intermediate. In some embodiments the invention contemplates employing an acetal or ketal instead of the carbonyl compound and polyol, wherein the acetal or ketal has been previously prepared from the polyol and carbonyl compound.

The structure or composition information about the carbonyl compound and polyol is readily ascertained and helpful for determining the polyol ether compound of formula (III) prepared therefrom. For example, the R^1 and R^2 are known from the carbonyl compound and Q, m, and R^3 to R^5 are known from the polyol, and so the Q, m, and R^1 to R^5 of the compound of formula (III) will be the same, respectively. Thus, R^1 and R^2 of preferred compounds of formula (III) are the same as the aforementioned preferred R^1 and R^2 of the carbonyl compound of formula (I) and Q, m, and R^3 to R^5 of the preferred compounds of formula (III) are the same as the aforementioned preferred Q, m, and R^3 to R^5 of the polyol of formula (II).

The acidic co-catalyst useful in the present invention can be characterized by type of acid and its pKa. In some embodiments the acidic co-catalyst comprises a type of acid commonly referred to as a Brønsted acid (i.e., a protic acid). Preferably the Brønsted acid has a pKa of 3 or less, more preferably 2.5 or less, and still more preferably 2.1 or less. A preferred Brønsted acid is phosphoric acid (H_3PO_4), trifluoroacetic acid, trifluoromethanesulfonic acid, *para*-toluenesulfonic acid, or camphorsulfonic acid. In some embodiments the acidic co-catalyst comprises a Lewis acid. Preferably the Lewis acid has a pKa of 3 or less. A preferred Lewis acid is $AlCl_3$ or BF_3 . In some embodiments of the process of the present invention one or more additional quantities of the acidic co-catalyst are added, periodically or continuously, to the reaction of the present invention to maintain or at least partially restore activity of the bimetal palladium hydrogenation catalyst, which activity can decrease over time in absence of such additional quantities. Continuous addition is preferred over periodic addition when conducting the present invention process in a continuous flow reactor. Periodic or continuous addition is useful when conducting the present invention process in a batch reactor.

The bimetal palladium hydrogenation catalyst useful in the present invention can be characterized by its at least one co-metal. In some embodiments there is one co-metal. In other embodiments there are two co-metals. In still other embodiments there are three co-metals. Preferably there are 5 or fewer co-metals.

In some embodiments the co-metal is any one of Ni, Ag, Fe, Cr, Mo, Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Ni and any one of Ag, Fe, Cr, Mo, Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Ag and any one of Fe, Cr, Mo, Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Fe and any one of Cr, Mo, Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Cr and any one of Mo, Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Mo and any one of Cu, Zn, Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Cu and any one of Zn,

Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Zn and any one of Mn, Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Mn and any one of Zr, W, and Au. In some embodiments the co-metal is selected from the group consisting of: Zr and any one of W and Au. In some embodiments the co-metal is W or Au. In some embodiments the co-metal is Ni(0). In some embodiments the co-metal is Ag(0). In some embodiments the co-metal is Fe(0). In some embodiments the co-metal is Cr(0). In some embodiments the co-metal is Mo(0). In some embodiments the co-metal is Cu(0). In some embodiments the co-metal is Zn(0). In some embodiments the co-metal is Mn(0). In some embodiments the co-metal is Zr(0). In some embodiments the co-metal is W(0). In some embodiments the co-metal is Au(0). In some embodiments the co-metal is a cation of La (e.g., La^{+3}) or Ce (e.g., Ce^{+1}). In some embodiments the co-metal is a cation of La (e.g., La^{+3}). In some embodiments the co-metal is a cation of Ce (e.g., Ce^{+1}).

The bimetal palladium hydrogenation catalyst useful in the present invention can be characterized by a weight percent of palladium, a weight percent of co-metal, or both, all based on total weight of the bimetal palladium hydrogenation catalyst, which characterization is referred to herein as catalyst composition. The invention contemplates any catalyst composition. Preferably the catalyst composition is from 0.01 wt% to 30 wt% of palladium based on total weight of the bimetal palladium hydrogenation catalyst (that is from 0.01 g to 30 g palladium per 100 g or the catalyst). More preferably the catalyst composition is from 0.1 wt% to 10 wt% palladium, and still more preferably 5 wt% palladium or less. Still more preferably the catalyst composition is 1 wt% palladium or more, and even more preferably 2 wt% palladium or more. Preferably the bimetal palladium hydrogenation catalyst comprises from 0.01 wt% to 20 wt% of the co-metal based on total weight of the bimetal palladium hydrogenation catalyst. More preferably the bimetal palladium hydrogenation catalyst comprises from 0.1 wt% to 10 wt% of the co-metal, and still more preferably 1 wt% co-metal or more, and even more preferably 2 wt% co-metal or more. In some embodiments the catalyst composition amounts of the palladium and co-metal independently are as described later in any one of the Examples.

The bimetal palladium hydrogenation catalyst useful in the present invention can be characterized by a ratio of weight palladium to weight of the co-metal, which characterization is referred to herein as catalyst metal weight/weight ratio. The invention contemplates any catalyst metal weight/weight ratio when the co-metal is silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium. Preferably the bimetal palladium hydrogenation catalyst is the bimetal palladium-(silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium) hydrogenation catalyst and is characterizable by a catalyst metal weight/weight ratio that is from 70 palladium: 30 (silver, iron, chromium, molybdenum, copper, zinc, manganese,

zirconium, tungsten, gold, lanthanum, or cerium) to 10 palladium:90 (silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium).

Preferably the catalyst metal weight/weight ratio is from 60 palladium:40 co-metal to 10 palladium:90 co-metal. More preferably the catalyst metal weight/weight ratio is from 57

- 5 palladium:43 co-metal to 20 palladium:80 co-metal. When the co-metal is nickel, the catalyst metal weight/weight ratio is from less than 50 palladium:greater than 50 nickel to 20 palladium:80 nickel. The catalyst metal weight/weight ratio can be conveniently calculated from the catalyst composition values. For example, a catalyst composition of 2.5 wt% palladium and 7.5 wt% co-metal gives a catalyst metal weight/weight ratio of 25:75 (i.e., 1:3)
- 10 Pd/co-metal and a catalyst composition of 5.0 wt% Pd and 3.7 wt% co-metal gives a catalyst metal weight/weight ratio of 57:43 Pd/co-metal. The catalyst weight/weight ratio values are based on total weight of the co-adsorption (i.e., a sum of weight of palladium plus weight(s) of all co-metal(s).

- The bimetal palladium hydrogenation catalyst useful in the present invention can be
- 15 characterized by a weight percent of catalyst per unit weight of the carbonyl compound, which characterization is referred to herein as catalyst loading. The invention contemplates any catalyst loading. Preferably the catalyst loading is from 0.1 wt% to 50 wt% of the bimetal palladium hydrogenation catalyst based on weight of the carbonyl compound (that is from 0.1 g to 50 g catalyst per 100 g of the carbonyl compound). More preferably the catalyst loading is from 1 wt%
- 20 to 40 wt%, still more preferably 25 wt% or less, and even more preferably 20 wt% or less. Still more preferably the catalyst loading is 2 wt% or more, and even more preferably 2.5 wt% or more. In some embodiments the catalyst loading is as described later in any one of the Examples.

- In some embodiments the carbon support is characterizable as having a Brunauer-Emmett-Teller (BET) surface area of 200 m²/g or greater. Preferably the BET surface area is 300
- 25 m²/g or greater, more preferably 500 m²/g or greater, and still more preferably 800 m²/g or greater. While the higher the BET surface area the better for this invention, in some embodiments the BET surface area is 2000 m²/g or less. In some embodiments the BET surface area is 1500 m²/g or less. In some embodiments the BET surface area is as described later in any one of the Examples.

- 30 The invention advantageously provides high yields of and greater molar selectivities for the polyol ether as described later herein. In some embodiments the invention process employs an excess amount of the polyol relative to the amount of the carbonyl compound wherein the excess amount is characterizable by a molar ratio of the polyol to the carbonyl compound that is greater than 5 moles of polyol per 1 mole of carbonyl compound (> 5:1). Such a >5:1 molar ratio
- 35 increases selectivity for a mono-ether form of the polyol ether over a di-ether form of the polyol

ether. Without being bound by theory, it is believed that use of the excess amount of the polyol leads to higher yields of the polyol ether (particularly the mono-ether form thereof) than if the amount of polyol relative to the amount of the carbonyl compound is 5:1 or less (e.g., 4:1, 3:1, 2:1, or less preferably, 1:1). The higher yields of the mono-ether form of the polyol ether due to the excess amount (i.e., >5:1) are believed to be due, at least in part, to creation of reaction conditions that reduce or eliminate by-product formation. In some embodiments the molar ratio of the polyol to the carbonyl compound is at least 6:1, in other embodiments at least 7:1, in still other embodiments at least 8:1, and in yet other embodiments at least 9:1. In some embodiments the molar ratio is about 10:1. There is no particular upper limit on the amount of excess polyol that is used, especially since the polyol can be recycled and reused. While it is believed the higher the molar ratio the higher the yields, in some embodiments practical considerations can place an upper limit on the molar ratio. In some embodiments the polyol to carbonyl compound molar ratio does not exceed 100:1, more preferably does not exceed 50:1, and still more preferably does not exceed 30:1. More preferably the molar ratio is from 7:1 to 30:1. A molar ratio of 5:1 or less increases selectivity for the di-ether form of the polyol ether over the mono-ether form of the polyol ether. In some embodiments the molar ratio is as described later in any one of the Examples.

A portion of the excess polyol can thus function as a solvent. Preferably the invention process does not employ a solvent other than the polyol, which is employed in greater than 5 molar ratio excess relative to the carbonyl compound as described previously. In some embodiments, however, the invention process further employs a solvent such as, for example, diethyl ether, tetrahydrofuran, 1,4-dioxane, or an ethylene end-capped polyalkylene glycol.

As previously mentioned, the invention advantageously provides high yields of the polyol ether. If the invention process is run for a sufficient time, preferably the process produces the polyol ether in greater than 70 percent yield, more preferably greater than 80 percent yield, still more preferably greater than 90 percent yield, and even more preferably greater than 92 percent yield, all based on the amount of the carbonyl compound. In some embodiments the percent yield is as described later in any one of the Examples.

As previously mentioned, the invention advantageously provides greater molar selectivities for the polyol ether. In some embodiments the molar selectivity is for the polyol ether over an alcohol by-product derived by reducing (adding hydrogen to) the carbonyl group of the carbonyl compound to give the corresponding alcohol by-product. In some embodiments the molar selectivity is for an intermediate acetal or ketal over the alcohol by-product. The intermediate acetal(s) or ketal(s) is derived from an *in situ* reaction of the carbonyl compound (R^1 is H and R^2 is not H in the case of the acetal(s) and both R^1 and R^2 are not H in the case of the ketal(s)) and the polyol with loss of a molecule of water, as illustrated later by a reaction scheme

in Representative Procedure 1. Preferably the process is characterizable by a molar selectivity ratio of greater than or equal to 3:1, more preferably greater than or equal to 6:1; still more preferably greater than or equal to 10:1; and even more preferably greater than or equal to 15:1 for producing the polyol ether over a potential alcohol by-product of formula (IV). More preferably the molar selectivity is greater than 3:1, still more preferably greater than 6:1, even more preferably greater than 10:1, and yet more preferably greater than 15:1. In some embodiments the molar selectivity ratio is as described later in any one of the Examples.

As mentioned previously, the bimetal palladium hydrogenation catalyst has been prepared by independent deposition-adsorption of a palladium salt and a corresponding co-metal salt, respectively, on the carbon support to give at least one deposited-adsorbed material, followed by an activating reduction of the at least one deposited-adsorbed material so as to produce the bimetal palladium hydrogenation catalyst. The term "palladium salt" means a net neutral ionic substance comprising a palladium cation and at least one anion. The term "co-metal salt" means a net neutral ionic substance comprising a co-metal cation and at least one anion. In the palladium salt and co-metal salt, the anions can be the same or different. Preferably each anion is an inorganic anion. More preferably each anion independently is a chloride, nitrate, acetate, hydroxide, oxide, or sulfate; and still more preferably chloride or nitrate. In some embodiments each of the palladium salt and at least one co-metal salt independently is as described later in the Examples.

As mentioned previously, the selective hydrogenating conditions mean reaction conditions such as environmental parameters and other reaction features under which a hydrogenation reaction is conducted that preferentially yields the polyol ether, or preferentially yields the aforementioned acetal(s) or ketal(s) intermediates, or preferably both. Examples of the environmental parameters are pressure, temperature, catalyst loading (as described previously), and presence or absence of ancillary ingredients such as, for example, solvent. Preferably pressure is from 50 pounds per square inch gauge (psig), i.e., 350 kilopascals (kPa) to 1000 psig (7,000 kPa). More preferably the pressure is from 400 psig (2800 kPa) to 1000 psi (7000 kPa). In some embodiments the pressure is as described later in any one of the Examples.

Preferably the temperature is from ambient temperature (i.e., 24 degrees Celsius (°C)) to 300 °C. More preferably the temperature is 250 °C or less and still more preferably 220 °C or less. Also more preferably the temperature is 100 °C or more, and still more preferably 150 °C or more. In some embodiments the temperature is as described later in any one of the Examples.

Examples of the other reaction features of the selective hydrogenating conditions are concentrations of reaction ingredients, presence or absence of additional additives, and reaction time. Concentrations of the carbonyl compound and palladium hydrogenation catalyst in the polyol depend upon how much excess polyol is employed. The invention process will work with

any concentrations of the carbonyl compound and bimetal palladium hydrogenation catalyst and such concentrations are not critical to the invention process. In some embodiments the concentrations are as described later in any one of the Examples.

5 In some embodiments the invention process is conducted in the absence of additives other than the acid co-catalyst. That is, the invention process contacts ingredients consisting essentially of the polyol, carbonyl compound, hydrogen gas, bimetal palladium hydrogenation catalyst, and acid co-catalyst. Use of additional additives is not critical to the invention process. In some embodiments the invention process further employs at least one additional additive, which preferably is a dehydrating agent. In some embodiments the additives are as described later
10 in any one of the Examples.

Preferably the invention process produces the at least 30% yield of the polyol ether within 12 hours, more preferably within 6 hours, still more preferably within 4 hours, and even more preferably within 2 hours reaction time. Preferably the invention process produces at least 50% yield, more preferably at least 70%, still more preferably at least 80%, and even more
15 preferably at least 90% yield of the polyol ether within 24 hours reaction time. More preferably the invention process produces the aforementioned yields within 6 hours, and still more preferably 4 hours reaction time. In some embodiments the yields and reaction times are as described later in any one of the Examples.

20 Materials and General Methods.

Surface area measurement protocol

Measure the Brunauer-Emmett-Teller (BET) surface area using a method in which 100% nitrogen, at thirteen different P/P_0 ratios is adsorbed onto a test sample at liquid nitrogen temperature. In the method, use a Micromeritics® multipoint BET surface area analyzer
25 (Micromeritics®, ASAP 2020). having a measurement position to make the measurements.

General method for B.E.T surface area is as below.

Weigh the apparatus at an ambient temperature for dry weight (I). Load the sample in the range of 0.5 gm to 1.2 gm in the sample tube and then insert the filler rod. Fit the seal frit and weigh the apparatus (II). Fix the sample tube to the degas port and attach the heating jacket to the
30 sample tube and plug it using a metal clip. Set the degas temperature to 300°C at a ramp rate of 10°C/min. The residence time at 300°C is considered to be at least 300 min. Detach the apparatus from the degassing unit at an ambient temperature and weigh the apparatus (III). Subtracting (I) from (III) will give the weight of the sample to be analyzed. Move the prepared sample to the analysis port. Attach an isothermal jacket and replace the sample tube to the analysis port. Fill the
35 Dewar with liquid N_2 . Perform the analysis at different P/P_0 values. Record signal readings in

square meters (m²). The BET surface area of 13 different P/Po is used to determine the final BET surface area.

Gas chromatograph instrument and protocol

- 5 A gas chromatographic method (GC) was used for the quantitative analysis of the reactants, intermediates, and products for reductive etherification of 1, 2-propylene glycol and n-butyraldehyde. Details of the method are given below in Table A.

Table A: GC parameters

GC instrument	Agilent 7890A
Column	HP-5 (J & W Scientific make), 30 meters, 0.32 millimeter (mm) inner diameter (i.d.); 0.25 micron (micrometer or μm) film thickness.
Temperature program	Initial temperature 50 °C, Hold time 2 minutes, rate of heating 20 °C/minute, final temperature 250 °C, Hold time 5 minutes.
Injector temperature	280 °C
Detector type	Flame ionization
Detector temperature	280 °C
Carrier gas	Helium
Carrier gas flow rate	1.5 mL/minute
Split ratio	50 : 1
Injection volume	1 microliter (μL)

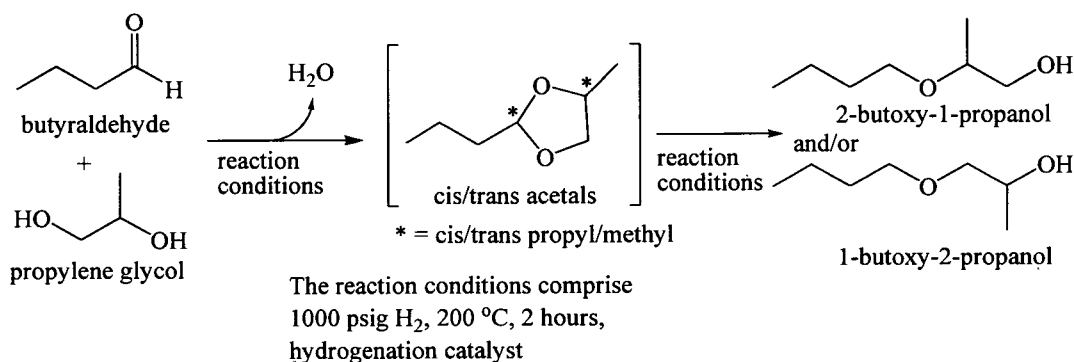
- 10 Preferred protocol for preparing the bimetal palladium hydrogenation catalyst

- Preferably the bimetal palladium hydrogenation catalyst has been prepared by deposition-adsorption. Contact a slurry of a mixture of PdCl₂ and a co-metal chloride in water to a carbon support to give a deposited-adsorbed material, followed by an activating reduction of the deposited-adsorbed material so as to produce the bimetal palladium hydrogenation catalyst,
- 15 wherein the co-metal is as defined previously. Preferably the activating reduction is performed by contacting together sodium borohydride and the deposited-adsorbed material at ambient temperature (e.g., 24 °C). More preferably the activating reduction is performed by contacting together hydrogen gas and the deposited-adsorbed material at ambient temperature (e.g., 24 °C) or higher and at pressures greater than atmospheric pressure. If desired remove water (e.g., by
- 20 drying at elevated temperature of 65 °C) from the resulting aqueous suspension of the bimetal palladium hydrogenation catalyst to give a dry form of the bimetal palladium hydrogenation catalyst.

Perform a preferred deposition-adsorption method as follows

Bimetal palladium hydrogenation catalyst has been prepared by deposition-adsorption. Calculated amount of PdCl_2 and a co-metal chloride are dissolved in water. The pH of resulting solution is adjusted by adding hydrochloric acid. The solution is stirred for 20 minutes. Carbon support is added to solution, and the resulting mixture is stirred for another 30 minutes to give a slurry of deposited-adsorbed material. Sodium borohydride solid, at ambient temperature (e.g., 24 °C) is slowly added to the slurry over a period of 5 minutes, and the resulting mixture is stirred for 30 minutes. The mixture is filtered and washed 4 times 30 mL with distilled water, and dried at 65 °C in static air.

- 10 Representative Procedure 1: Synthesizing 2-butoxy-1-propanol and/or 1-butoxy-2-propanol (polyol ethers) from propylene glycol (polyol), butyraldehyde (carbonyl compound) and hydrogen gas in the presence of a hydrogenation catalyst.



- Carry out the reaction in a 300 mL volumed stirred Parr autoclave. In a typical experiment, 0.332 g of hydrogenation catalyst, butyraldehyde (7.5 mL, 6.0 g, 0.083 mol) and 1,2-propylene glycol (93 mL, 1.3 mol of propylene glycol, acidified with phosphoric acid to pH of 5) (a molar ratio of polyol to carbonyl compound of 16:1) are poured into the autoclave, and an initial sample is withdrawn. The autoclave is closed and flushed first with nitrogen gas (300 psi; 2100 kPa) and then with hydrogen gas. An initial hydrogen gas pressure of 500 psig (3500 kPa) is maintained, and the temperature is increased to 200 °C (a desired temperature) with slow stirring to ensure a uniform temperature in the reactor. Under these conditions the hydrogen gas pressure is found to increase by about 150 psig (1100 kPa) to 200 psig (1400 kPa) to an increased pressure of around 650 psig (4600 kPa) to 700 psig (4900 kPa). The autoclave is then filled to a pressure of 1000 psig (7000 kPa) with hydrogen gas, and the stirring is increased to 1000 revolutions per minute (rpm). The reaction is continued for 2 hours. After 2 hours cool the reactor and its contents, release residual hydrogen gas, and flush the reactor with nitrogen before opening the reactor. Analyze a sample of the cooled and flushed reaction mixture by gas chromatography as described previously to measure amounts of 1-butoxy-2-

propanol and/or 2-butoxy-1-propanol and any intermediates and by-products (e.g., 1-butanol and dibutyl ether).

Non-limiting examples of the present invention are described below that illustrate some specific embodiments and aforementioned advantages of the present invention. Preferred
 5 embodiments of the present invention incorporate one limitation, and more preferably any two, limitations of the Examples, which limitations thereby serve as a basis for amending claims.

Example(s) of the Present Invention.

Examples 1 to 3 (EX-1 to EX-3): synthesis of a bimetal catalyst that is a bimetallic catalyst of 5
 10 wt% Pd and 5 wt% co-metal Ni (EX-1); 2.5 wt% Pd and 7.5 wt% co-metal Ni (EX-2); or 1 wt% Pd and 9 wt% co-metal Ni (EX-3); all on carbon support.

EX-1: PdCl_2 (83 mg (50.0 mg Pd^{+2}); Aldrich 08625JH 5G M.W 177.31) is dissolved in 150 mL distilled water by addition of 0.05 mL to 0.1 mL of HCl to get a clear solution. Add
 15 NiCl_2 (Rankem, Batch no. P184F07, M.W.237.71, 187 mg) to the clear solution and then carbon support (Rankem, product code: C0155, A.W.12.01, 900 mg). Stir the resulting mixture for 2 hours. Add sodium borohydride (NaBH_4 , Spectrochem, Lot no. S40223-067, 264 mg) slowly to the resulting solution and stir until dissolution is complete. Filter the resulting mixture and wash the resulting filtercake thoroughly three to four times with distilled water and dry under vacuum at 65° C to give the bimetallic catalyst of EX-1. A suspension in water of catalyst of EX-1
 20 produces a pH from pH 7 to pH 8.

EX-2: Repeat the procedure of Example 1 except us 41.5 mg PdCl_2 and 281 mg of NiCl_2 to give the bimetallic catalyst of EX-2.

EX-3: Repeat the procedure of Example 1 except us 16.6 mg PdCl_2 and 337 mg of NiCl_2 to give the bimetallic catalyst of EX-3.

25 Examples 4 and 5 (EX-4 and EX-5): synthesis of a bimetal catalyst that is 5 wt% Pd and 7.5 wt% co-metal La^{+3} (EX-4); or 5 wt% Pd and 7.5 wt% co-metal Ce^{+1} (EX-5); both on carbon support.

EX-4: Add $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2339 g; S.D. Fine) to 100 mL water and then activated
 30 carbon (RANKEM, Batch No P083D08, 900 mg). Stir for 30 minutes to give a first solution. Slowly add solid NaBH_4 (264 mg) to the first solution. Observe evolution of hydrogen gas. Stir for 30 minutes, filter the resulting reaction mixture, and wash the resulting first filtercake many times with distilled water. Dry the resulting first washed sample at 100 °C in static air to give a first dried material. Dissolve calculated amount of PdCl_2 (ALDRICH , Lot no S439554 – 357,

- 83.3 mg) in 100 mL water by adding two drops of concentrated hydrochloric acid thereto. Add the first dried material to the resulting palladium chloride solution. Stir for 30 minutes to give a second solution. Slowly add solid NaBH_4 (264 mg) to the second solution. Observe evolution of hydrogen gas. Stir for 30 minutes, filter the resulting reaction mixture, and wash the resulting second filtercake many times with distilled water. Dry the resulting second washed sample at 100 °C in static air to give the bimetal catalyst of EX-4.

EX-5: Repeat the procedure of EX-4 except use $\text{CeNO}_3 \cdot 6\text{H}_2\text{O}$ (0.2328 g; Acros Organics) instead of the $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to give the bimetal catalyst of EX-5.

- Examples 6 to 16 (EX-6 and EX-16): synthesis of a bimetal catalyst that is a bimetallic catalyst that is 5 wt% Pd and 10 wt% of a co-metal (or 13.7 wt% Ag or 3.7 wt% W) that is: Mo (EX-6); Zr (EX-7); Fe (EX-8); Cr (EX-9); Mn (EX-10); Cu (EX-11); Au (EX-12); Zn (EX-13); 13.7 wt% Ag (EX-14), 3.7 wt% W (EX-15); or 10 wt% W (EX-16); all on carbon support.

- General procedure: Separately repeat the procedure of EX-4 ten times except each time use a different one of the metal salt starting materials and amounts thereof indicated below in Table 1 instead of the $\text{La(NO}_3)_3$ to give a different one of the bimetal catalysts of EX-6 to EX-16, respectively.

Table 1: form of metal salt starting material and amount used

Example Number	Catalyst	Metal salt (commercial source)	Amount used (g)
EX-6	5 wt% Pd-10 wt% Mo/Carbon	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (S.D. Fine)	0.1787
EX-7	5 wt% Pd-10 wt% Zr /Carbon	$\text{ZrO(NO}_3)_2$ (Acros Organic)	0.2535
EX-8	5 wt% Pd-10 wt% Fe/Carbon	$\text{Fe(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Chemport)	0.5156
EX-9	5 wt% Pd-10 wt% Cr/Carbon	$\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros Organics)	0.7696
EX-10	5 wt% Pd-10 wt% Mn/Carbon	$\text{Mn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich Chemical)	0.5225
EX-11	5 wt% Pd-10 wt% Cu/Carbon	$\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (S.D. Fine)	0.3802
EX-12	5 wt% Pd-10 wt% Au/Carbon	$\text{HAuCl}_2 \cdot 3\text{H}_2\text{O}$ (Aldrich Chemical)	0.1999
EX-13	5 wt% Pd-10 wt% Zn/Carbon	$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (S.D. Fine)	0.4549
EX-14	5 wt% Pd-13.7 wt% Ag/Carbon	AgNO_3 (S.D. Fine)	0.2150

EX-15	5 wt% Pd-3.7 wt% W/Carbon	(NH ₄) ₁₀ H ₂ (W ₂ O ₇) ₆ (Aldrich Chemical)	0.6232
EX-16	5 wt% Pd-10 wt% W/Carbon	(NH ₄) ₁₀ H ₂ (W ₂ O ₇) ₆ (Aldrich Chemical)	1.6653

- Examples A to P (EX-A to EX-P, respectively): synthesizing 2-butoxy-1-propanol and/or 1-butoxy-2-propanol from propylene glycol, butyraldehyde and hydrogen gas in the presence of the invention bimetal hydrogenation catalyst of EX-1 to EX-16, respectively.

Repeat the aforementioned Representative Procedure 1 using the bimetallic catalyst of EX-1 to EX-16 respectively. Results are reported below in Table 2.

Table 2: gas chromatography results of synthesis of 2-butoxy-1-propanol and/or 1-butoxy-2-propanol according to EX-A to EX-P.

EX no. (catalyst)	Consumption of butyraldehyde (%)	Total yield of cis/trans acetals + polyol ethers (%)	Percent Yields (%) (Selectivities = % yield poly ethers or cis/trans acetals divided by % yield 1-butanol)		
			1-Butanol	cis/trans acetals	Poly ethers: 2- butoxy-1- propanol and/or 1-butoxy-2- propanol
EX-A (5 wt% Pd-5 wt% Ni/Carbon)	100	90.5	9.47	33.44 (3.5)	57.08 (6.0)
EX-B (2.5 wt% Pd-7.5 wt% Ni/Carbon)	98	88	12	51 (4.2)	37 (3.1)
EX-C (1 wt% Pd-9 wt% Ni/Carbon)	89	52	20	49	3
EX-D (5 wt% Pd-7.5 wt% La ⁺³ /Carbon)	100	85	5	13 (2.6)	82 (16)
EX-E (5 wt% Pd-7.5 wt% Ce ⁺¹ /Carbon)	100	94	6	18 (3)	76 (13)
EX-F (5 wt% Pd-10 wt% Mo/Carbon)	100	89	11	27	62
EX-G (5 wt% Pd-10 wt% Zr/Carbon)	100	92	8	32	60
EX-H (5 wt% Pd-10 wt% Fe/Carbon)	100	93	7	41	52
EX-I (5 wt% Pd-10 wt%	100	96	4	44	52

Cr/Carbon)					
EX-J (5 wt% Pd-10 wt% Mn/Carbon)	100	83	18	26	57
EX-K (5 wt% Pd-10 wt% Cu/Carbon)	100	81	19	39	42
EX-L (5 wt% Pd-10 wt% Au/Carbon)	100	91	9	41	50
EX-M (5 wt% Pd-10 wt% Zn/Carbon)	100	83	18	52	31
EX-N (5 wt% Pd-10 wt% Ag/Carbon)	100	95	5	82	13
EX-O (5 wt% Pd-3.7 wt% W/Carbon)	100	95	7	37	58
EX-P (5 wt% Pd-10 wt% W/Carbon)	100	96	4	37	59

As seen from the data in Table 2, the invention catalysts produce the polyol ethers or cis/trans acetals and polyol ethers in high yield and high selectivity over the undesired 1-butanol by-product. Accordingly, the invention process advantageously produces the polyol ether in high yields (greater than 50% yield after only 2 hours) and greater molar selectivities (6:1 or more) for polyol ethers over alcohol by-products, which typically are the primary by-products and are derived from undesired reduction of the carbonyl compound. The invention also advantageously produces the intermediate cis/trans acetals in greater molar selectivities over the alcohol by-products. Conducting the Representative Procedure 1 with an invention bimetal palladium hydrogenation catalyst and for longer than the aforementioned 2 hours (e.g., 4 hours or more) advantageously will further increase yields of the polyol ethers and molar selectivities for the polyol ethers over the alcohol by-products.

The invention discovered the *in situ* formation of intermediate acetal or ketal from dehydrating condensation of the polyol and carbonyl compound produces the polyol ether in higher yields and selectivities than corresponding reactions employing the acetal or ketal in place of the carbonyl compound. The invention discovered that the bimetal palladium hydrogenation catalyst facilitates increased catalytic activity thereof compared to other palladium catalysts that lack the co-metal feature thereof and have a same palladium composition weight percent, and even compared to bimetallic palladium catalysts that have been prepared by methods other than the instant deposition-adsorption/reduction. The higher yields of and increased selectivities for the polyol ethers makes the invention process especially valuable in the preparation of polyol

ethers for use as, for example, solvents, surfactants, wetting agents, emulsifying agents, lubricants, and intermediates for the preparation of surfactants.

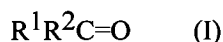
5 While the invention has been described above according to its preferred embodiments, it can be modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the instant invention using the general principles disclosed herein. Further, the instant application is intended to cover such departures from the present disclosure as come within the known or customary practice in the art to which this invention pertains and which fall within the limits of the following claims.

CLAIMS

What is claimed is:

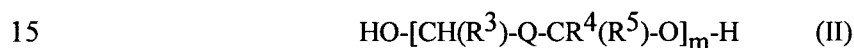
1. A process for making a polyol ether, the process comprising contacting together under selective hydrogenating conditions an amount of a polyol, an amount of a carbonyl compound, an excess amount of hydrogen gas, a catalytic amount of a bimetal palladium hydrogenation catalyst, and an acidic co-catalyst so as to provide the polyol ether, wherein:

(a) the carbonyl compound is of formula (I):



- 10 wherein each of R^1 and R^2 independently is hydrogen atom (H), (C₁-C₅₀)alkyl, (C₂-C₅₀)alkenyl, (C₆-C₁₀)aryl-(C₁-C₅₀)alkyl, (C₆-C₁₀)aryl-(C₂-C₅₀)alkenyl-, or (C₃-C₁₂)cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a (C₃-C₁₂)cycloalkyl ring;

(b) the polyol is a compound of formula (II):

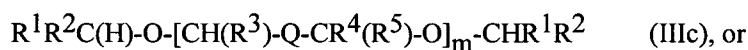
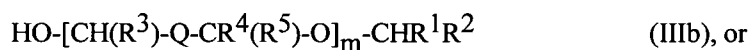
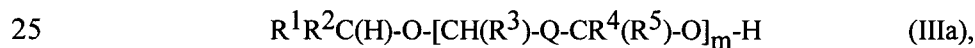


wherein m is an integer of from 1 to 2000;

each Q independently is a covalent bond, L, X, L-X, X-L, or L-X-L, wherein each L independently is (C₁-C₁₄)alkylene, (C₁-C₁₄)heteroalkylene, or (C₂-C₁₄)alkenylene; and each X independently is (C₃-C₁₂)cycloalkylene, (C₂-C₁₂)heterocycloalkylene, (C₆-C₁₀)arylene, or (C₁-C₁₀)heteroarylene;

20 each of R^3 , R^4 , and R^5 independently is H, (C₁-C₂₀)alkyl, (C₆-C₁₀)aryl-(C₁-C₁₀)alkyl, or (C₃-C₁₂)cycloalkyl; or R^4 and R^5 are together with the carbon atom to which they are both attached form a (C₃-C₁₂)cycloalkyl ring;

(c) the polyol ether comprises a compound of formula (IIIa), (IIIb), or (IIIc):



a mixture of any two or more compounds of the formulas (IIIa), (IIIb), and (IIIc),

wherein R^1 and R^2 independently is hydrogen atom (H), (C₁-C₅₀)alkyl, (C₆-

30 C₁₀)aryl-(C₁-C₅₀)alkyl, or saturated (C₃-C₁₂)cycloalkyl; or R^1 and R^2 together with

the carbon atom to which they are both attached form a saturated (C₃-C₁₂)cycloalkyl ring; each Q independently is a covalent bond, L, X, L-X, X-L, or L-X-L, wherein each L independently is (C₁-C₁₄)alkylene or saturated (C₁-C₁₄)heteroalkylene; and each X independently is a saturated (C₃-C₁₂)cycloalkylene, saturated (C₂-C₁₂)heterocycloalkylene, (C₆-C₁₀)arylene, or (C₁-C₁₀)heteroarylene; and m, and R³ to R⁵ are as defined previously; and

in (a) to (c) each alkyl, alkylene, alkenyl, alkenylene, aryl, arylene, cycloalkyl, cycloalkylene, (C₁-C₁₄)heteroalkylene, and (C₂-C₁₂)heterocycloalkylene group independently is unsubstituted or substituted with from 1 to 10 substituent groups R^S;

each R^S is bonded to a carbon atom and independently is a hydroxyl (-OH), =O, halo, di(C₁-C₂₀)alkylamino, (C₁-C₆)alkyl, -CHO (i.e., -C(=O)-H), -CO(C₁-C₆)alkyl (i.e., -C(=O)-(C₁-C₆)alkyl), -CO₂H, -CO₂(C₁-C₆)alkyl, -CON((C₁-C₆)alkyl)₂, (C₁-C₆)alkoxy, (C₂-C₆)alkynyl, or -SH;

(d) the bimetal palladium hydrogenation catalyst comprises a co-adsorption of palladium and at least one co-metal that is nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium, the palladium-(co-metal) residing on a carbon support; the bimetal palladium-nickel hydrogenation catalyst being characterizable by a catalyst metal weight/weight ratio that is from less than 50 palladium:greater than 50 nickel to 20 palladium:80 nickel; the palladium hydrogenation catalyst having been prepared by independent deposition-adsorption of a palladium salt and a corresponding co-metal salt, respectively, on the carbon support to give at least one deposited-adsorbed material, followed by an activating reduction of the at least one deposited-adsorbed material so as to produce the bimetal palladium hydrogenation catalyst; and

(e) the process produces the polyol ether in at least 30 percent yield based on the amount of the carbonyl compound and the process is characterizable by a molar selectivity ratio of greater than 10:1 for producing the polyol ether over a potential alcohol by-product of formula (IV) R¹R²CHOH (IV), wherein R¹ and R² are as defined previously.

2. The process as in claim 1, the process being further characterizable by any one or more of limitations (a) to (m):

(a) the selective hydrogenating conditions comprise a pressure of from 100 kilopascals to 14,000 kilopascals and a temperature of from 24 degrees Celsius to 300 degrees Celsius;

- (b) the bimetal palladium hydrogenation catalyst is characterized by a catalyst composition of from 0.01 wt% to 30 wt% of palladium and from 0.1 wt% to 20 wt% of the co-metal based, both based on total weight of the palladium hydrogenation catalyst;
- (c) the bimetal palladium hydrogenation catalyst is the bimetal palladium-nickel hydrogenation catalyst and is characterized by a catalyst metal weight/weight ratio of from 40 palladium:60 nickel to 20 palladium:80 nickel; or the bimetal palladium hydrogenation catalyst is the bimetal palladium-(silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium) hydrogenation catalyst and is characterizable by a catalyst metal weight/weight ratio that is from 70 palladium: 30 (silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium) to 10 palladium:90 (silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium);
- (d) the bimetal palladium hydrogenation catalyst is characterized by a catalyst loading of from 0.1 wt% to 50 wt% of the bimetal palladium hydrogenation catalyst based on weight of the carbonyl compound;
- (e) the acidic co-catalyst comprises a Brønsted acid having an acid dissociation constant (pKa) of 3 or less;
- (f) the molar ratio of the polyol to the carbonyl compound is from greater than 5:1 to 30:1;
- (g) the process is characterizable by a molar selectivity ratio of greater than 20:1 for producing the polyol ether over a potential alcohol by-product of formula (IV) R^1R^2CHOH (IV), wherein R^1 and R^2 are as defined previously;
- (h) the process produces the polyol ether in greater than 70 percent yield within 12 hours of reaction time;
- (i) the at least one co-metal comprises a co-metal(0) wherein the co-metal is nickel;
- (j) the at least one co-metal comprises a co-metal(0) wherein the co-metal is silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, or gold;
- (k) the at least one co-metal comprises a cation of lanthanum or cerium;
- (l) the carbon support is characterizable as having a Brunauer-Emmett-Teller surface area of 200 square meters per gram or greater; and
- (m) the process contacts together ingredients consisting essentially of the polyol, carbonyl compound, hydrogen gas, and palladium hydrogenation catalyst.
3. The process as in claim 2, the process being characterizable by at least each of limitations (a) to (c) and limitation (d).

4. The process as in claim 2 or 3, the process being characterizable by at least each of limitations (a) to (c) and limitation (e).
5. The process as in any one of claims 2 to 4, the process being characterizable by at least each of limitations (a) to (c) and limitation (f).
- 5 6. The process as in any one of claims 2 to 5, the process being characterizable by at least each of limitations (a) to (c) and limitation (g).
7. The process as in any one of claims 2 to 6, the process being characterizable by at least each of limitations (a) to (c) and limitation (h).
8. The process as in any one of claims 2 to 7, the process being characterizable by at least each of limitations (a) to (c) and limitation (i).
- 10 9. The process as in any one of claims 2 to 8, the process being characterizable by at least each of limitations (a) to (c) and limitation (j).
10. The process as in any one of claims 2 to 9, the process being characterizable by at least each of limitations (a) to (c) and limitation (k).
- 15 11. The process as in any one of claims 2 to 10, the process being characterizable by at least each of limitations (a) to (c) and limitation (l).
12. The process as in any one of claims 2 to 11, the process being characterizable by at least each of limitations (a) to (c) and limitation (m).
13. The process as in any one of claims 1 to 12, wherein in formula (I) one of R^1 and R^2 is H and the other of R^1 and R^2 is (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl-, or (C_3-C_{12}) cycloalkyl; and in formula (III) one of R^1 and R^2 is H and the other of R^1 and R^2 is (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl.
- 20 14. The process as in any one of claims 1 to 12, wherein in formula (I) each one of R^1 and R^2 independently is (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl-, or (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring; and in formula
- 25

(III) each one of R^1 and R^2 independently is (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a saturated (C_3-C_{12}) cycloalkyl ring.

15. The process as in any one of claims 1 to 14, wherein each Q is a covalent bond.

5 16. The process as in any one of claims 1 to 14, wherein in formula (II) each Q independently is (C_1-C_{14}) alkylene or (C_1-C_{14}) heteroalkylene; and in formula (III) each Q independently is (C_1-C_{14}) alkylene or saturated (C_1-C_{14}) heteroalkylene.

17. The process as in any one of claims 1 to 16, wherein m is 1.

18. The process as in any one of claims 1 to 16, wherein m is from 2 to 100.

10 19. A process for preparing a bimetal palladium hydrogenation catalyst, the process comprising:

15 independently depositing-adsorbing a palladium salt and a corresponding co-metal salt that is a salt of nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium on a carbon support to give at least one deposited-adsorbed material; and

20 activatingly reducing the at least one deposited-adsorbed material so as to produce a bimetal palladium hydrogenation catalyst comprising a co-adsorption of palladium and at least one co-metal that is nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium, the palladium-(co-metal) residing on the carbon support; the depositing-adsorbing steps can be performed sequentially or essentially simultaneously; and the activatingly reducing steps can be performed sequentially or essentially simultaneously.

20. A process as in claim 19, wherein the carbon support is characterizable as having a Brunauer-Emmett-Teller of $200 \text{ m}^2/\text{g}$ or greater.

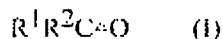
25 21. A bimetal palladium hydrogenation catalyst prepared by the process as in claim 19 or 20.

AMENDED CLAIMS

received by the International Bureau on 02 May 2011 (02.05.2011)

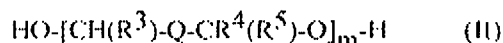
1. A process for making a polyol ether, the process comprising contacting together under selective hydrogenating conditions an amount of a polyol, an amount of a carbonyl compound, an excess amount of hydrogen gas, a catalytic amount of a bimetal palladium hydrogenation catalyst, and an acidic co-catalyst so as to provide the polyol ether, wherein:

(a) the carbonyl compound is of formula (I);



wherein each of R^1 and R^2 independently is hydrogen atom (H), (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl, or (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring;

(b) the polyol is a compound of formula (II);

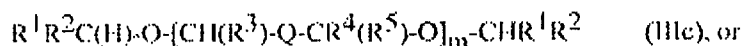
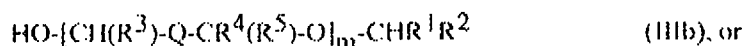
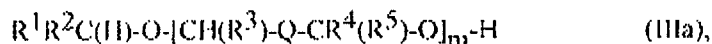


wherein m is an integer of from 1 to 2000;

each Q independently is a covalent bond, L, X, L-X, X-L, or L-X-L, wherein each L independently is (C_1-C_{14}) alkylene, (C_1-C_{14}) heteroalkylene, or (C_2-C_{14}) alkenylene; and each X independently is (C_3-C_{12}) cycloalkylene, (C_2-C_{12}) heterocycloalkylene, (C_6-C_{10}) arylene, or (C_1-C_{10}) heteroarylene;

each of R^3 , R^4 , and R^5 independently is H, (C_1-C_{20}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{10}) alkyl, or (C_3-C_{12}) cycloalkyl; or R^4 and R^5 are together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring;

(c) the polyol ether comprises a compound of formula (IIIa), (IIIb), or (IIIc):



a mixture of any two or more compounds of the formulas (IIIa), (IIIb), and (IIIc),

wherein R^1 and R^2 independently is hydrogen atom (H), (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a saturated (C_3-C_{12}) cycloalkyl ring; each Q independently is a covalent bond, L, X, L-X, X-L, or L-X-L, wherein each L independently is

(C₁-C₁₄)alkylene or saturated (C₁-C₁₄)heteroalkylene; and each X independently is a saturated (C₃-C₁₂)cycloalkylene, saturated (C₂-C₁₂)heterocycloalkylene, (C₆-C₁₀)arylene, or (C₁-C₁₀)heteroarylene; and m, and R³ to R⁵ are as defined previously; and

in (a) to (c) each alkyl, alkylene, alkenyl, alkenylene, aryl, arylene, cycloalkyl, cycloalkylene, (C₁-C₁₄)heteroalkylene, and (C₂-C₁₂)heterocycloalkylene group independently is unsubstituted or substituted with from 1 to 10 substituent groups R⁸;

each R⁸ is bonded to a carbon atom and independently is a hydroxyl (-OH), -O-, halo, di(C₁-C₂₀)alkylamino, (C₁-C₆)alkyl, -CHO (i.e., -C(=O)-H), -CO(C₁-C₆)alkyl (i.e., -C(=O)-(C₁-C₆)alkyl), -CO₂H, -CO₂(C₁-C₆)alkyl, -CON((C₁-C₆)alkyl)₂, (C₁-C₆)alkoxy, (C₂-C₆)alkynyl, or -SH;

(d) the bimetal palladium hydrogenation catalyst comprises a co-adsorption of palladium and at least one co-metal that is nickel, silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium, the palladium-(co-metal) residing on a carbon support: the bimetal palladium-nickel hydrogenation catalyst being characterizable by a catalyst metal weight/weight ratio that is from less than 50 palladium:greater than 50 nickel to 20 palladium:80 nickel; the palladium hydrogenation catalyst having been prepared by independent deposition-adsorption of a palladium salt and a corresponding co-metal salt, respectively, on the carbon support to give at least one deposited-adsorbed material, followed by an activating reduction of the at least one deposited-adsorbed material so as to produce the bimetal palladium hydrogenation catalyst; and

(e) the process produces the polyol ether in at least 30 percent yield based on the amount of the carbonyl compound and the process is characterizable by a molar selectivity ratio of greater than 3:1 for producing the polyol ether over a potential alcohol by-product of formula (IV) R¹R²CHOH (IV), wherein R¹ and R² are as defined previously.

2. The process as in claim 1, the process being further characterizable by any one or more of limitations (a) to (m):
 - (a) the selective hydrogenating conditions comprise a pressure of from 100 kilopascals to 14,000 kilopascals and a temperature of from 24 degrees Celsius to 300 degrees Celsius;
 - (b) the bimetal palladium hydrogenation catalyst is characterized by a catalyst composition of from 0.01 wt% to 30 wt% of palladium and from 0.1 wt% to 20 wt% of the co-metal based, both based on total weight of the palladium hydrogenation catalyst;
 - (c) the bimetal palladium hydrogenation catalyst is the bimetal palladium-nickel hydrogenation catalyst and is characterized by a catalyst metal weight/weight ratio of from 40 palladium:60 nickel to 20 palladium:80 nickel; or the bimetal palladium hydrogenation

- catalyst is the bimetal palladium-(silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium) hydrogenation catalyst and is characterizable by a catalyst metal weight/weight ratio that is from 70 palladium:30 (silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium) to 10 palladium:90 (silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, gold, lanthanum, or cerium);
- (d) the bimetal palladium hydrogenation catalyst is characterized by a catalyst loading of from 0.1 wt% to 50 wt% of the bimetal palladium hydrogenation catalyst based on weight of the carbonyl compound;
- (e) the acidic co-catalyst comprises a Bronsted acid having an acid dissociation constant (pKa) of 3 or less;
- (f) the molar ratio of the polyol to the carbonyl compound is from greater than 5:1 to 30:1;
- (g) the process is characterizable by a molar selectivity ratio of greater than 6:1 for producing the polyol ether over a potential alcohol by-product of formula (IV) R^1R^2CHOH (IV), wherein R^1 and R^2 are as defined previously;
- (h) the process produces the polyol ether in greater than 70 percent yield within 12 hours of reaction time;
- (i) the at least one co-metal comprises a co-metal(0) wherein the co-metal is nickel;
- (j) the at least one co-metal comprises a co-metal(0) wherein the co-metal is silver, iron, chromium, molybdenum, copper, zinc, manganese, zirconium, tungsten, or gold;
- (k) the at least one co-metal comprises a cation of lanthanum or cerium;
- (l) the carbon support is characterizable as having a Brunauer-Emmett-Teller surface area of 200 square meters per gram or greater; and
- (m) the process contacts together ingredients consisting essentially of the polyol, carbonyl compound, hydrogen gas, and palladium hydrogenation catalyst.
3. The process as in claim 2, the process being characterizable by at least each of limitations (a) to (c) and limitation (d).
 4. The process as in claim 2 or 3, the process being characterizable by at least each of limitations (a) to (c) and limitation (e).
 5. The process as in any one of claims 2 to 4, the process being characterizable by at least each of limitations (a) to (c) and limitation (f).
 6. The process as in any one of claims 2 to 5, the process being characterizable by at least each of limitations (a) to (c) and limitation (g).

7. The process as in any one of claims 2 to 6, the process being characterizable by at least each of limitations (a) to (c) and limitation (h).
8. The process as in any one of claims 2 to 7, the process being characterizable by at least each of limitations (a) to (c) and limitation (i).
9. The process as in any one of claims 2 to 8, the process being characterizable by at least each of limitations (a) to (c) and limitation (j).
10. The process as in any one of claims 2 to 9, the process being characterizable by at least each of limitations (a) to (c) and limitation (k).
11. The process as in any one of claims 2 to 10, the process being characterizable by at least each of limitations (a) to (c) and limitation (l).
12. The process as in any one of claims 2 to 11, the process being characterizable by at least each of limitations (a) to (c) and limitation (m).
13. The process as in any one of claims 1 to 12, wherein in formula (I) one of R^1 and R^2 is H and the other of R^1 and R^2 is (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl-, or (C_3-C_{12}) cycloalkyl; and in formula (II) one of R^1 and R^2 is H and the other of R^1 and R^2 is (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl.
14. The process as in any one of claims 1 to 12, wherein in formula (I) each one of R^1 and R^2 independently is (C_1-C_{50}) alkyl, (C_2-C_{50}) alkenyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_2-C_{50}) alkenyl-, or (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a (C_3-C_{12}) cycloalkyl ring; and in formula (II) each one of R^1 and R^2 independently is (C_1-C_{50}) alkyl, (C_6-C_{10}) aryl- (C_1-C_{50}) alkyl, or saturated (C_3-C_{12}) cycloalkyl; or R^1 and R^2 together with the carbon atom to which they are both attached form a saturated (C_3-C_{12}) cycloalkyl ring.
15. The process as in any one of claims 1 to 14, wherein each Q is a covalent bond.

16. The process as in any one of claims 1 to 14, wherein in formula (II) each Q independently is (C₁-C₁₄)alkylene or (C₁-C₁₄)heteroalkylene; and in formula (III) each Q independently is (C₁-C₁₄)alkylene or saturated (C₁-C₁₄)heteroalkylene.
17. The process as in any one of claims 1 to 16, wherein m is 1.
18. The process as in any one of claims 1 to 16, wherein m is from 2 to 100.
19. The process as in any one of the preceding claims, wherein the molar selectivity ratio is greater than 10:1.

STATEMENT UNDER ARTICLE 19 (1)

Claims 19 to 21 are cancelled.

Claim 1 has been amended by deleting the molar selectivity ratio "10:1" and inserting instead "3:1". The molar selectivity ratio in claim 1 will thus be greater than 3:1. Support for the same can be found in the specification on page 18, line 5.

Claim 2 has been amended by deleting the molar selectivity ratio in limitation (g) "20:1" and inserting instead "6:1". The molar selectivity ratio in limitation (g) in claim 2 will thus be greater than 6:1. Support for the same can be found in the specification on page 18, line 5.

New claim 19 is added to the claim set. Support for the same can be found in original claim 1 and in the specification on page 18, line 6.

We request the International Bureau to take these amendments on record and to proceed further.

Kindly acknowledge receipt of this letter and the attachments.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2010/000106

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D317/12	C07C41/09	B01J23/63	B01J23/89	B01J35/10
B01J21/18	B01J23/44	B01J23/48	B01J23/50	B01J23/52
B01J23/60	B01J23/652	B01J23/656	B01J37/02	B01J37/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 446 210 A (HEES UDO [DE] ET AL) 29 August 1995 (1995-08-29) cited in the application * abstract column 1, line 64 - column 2, line 8 column 2, line 31 - line 52 claims 1-20 examples 1-5	1-18
X	----- YAKOVLEV ET AL: "Kinetic study of liquid-phase hydrodechlorination of hexachlorobenzene on Ni/C and 2%PdNi/C", KINETICS AND CATALYSIS, vol. 41, 2000, pages 25-32, XP002623876, page 25, column 2, paragraphs 2,5 ----- -/-	19-21

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

21 February 2011

Date of mailing of the international search report

07/03/2011

Name and mailing address of the ISA/

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Authorized officer

Eberhard, Michael

INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2010/000106

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 300 528 A (RYOICHI WAKASA ET AL) 24 January 1967 (1967-01-24) examples 1,4,10 -----	19-21
X	GB 832 141 A (GEN ANILINE & FILM CORP) 6 April 1960 (1960-04-06) example I -----	19-21
X	US 5 447 896 A (RAO V N MALLIKARJUNA [US]) 5 September 1995 (1995-09-05) examples 1,4 -----	19-21
X	US 5 473 086 A (BUDGE JOHN R [US] ET AL) 5 December 1995 (1995-12-05) examples 1,3,B claims 1-16 -----	19-21
X	EP 0 644 173 A1 (DAIKIN IND LTD [JP]) 22 March 1995 (1995-03-22) examples 15,16,18-20,22,23 -----	19-21
X	CN 1 460 549 A (DALIAN ZHENBENG FLUOROCOATING [CN]) 10 December 2003 (2003-12-10) * Comparative example 5, sample F * * Comparative example 6, sample G * examples 1-42 -----	19-21
X	JP 2004 074061 A (OTSUKA KIYOSHI; UCHIYA THERMOSTAT) 11 March 2004 (2004-03-11) paragraphs [36 Pd] - [Ni/GrCF] -----	19-21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2010/000106

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/ IN2010/ 000106

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18

A process for making a polyol ether, the process comprising contacting together under selective hydrogenating conditions an amount of a polyol, an amount of a carbonyl compound, an excess amount of hydrogen gas, a catalytic amount of a bimetal palladium hydrogenation catalyst, and an acidic co-catalyst so as to provide the polyol ether.

2. claims: 19-21

A bimetal palladium hydrogenation catalyst and a process for preparing a bimetal palladium hydrogenation catalyst.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2010/000106

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US 5473086	A	05-12-1995	AT 178878 T CN 1129206 A DE 69509060 D1 DE 69509060 T2 EP 0722923 A2 ES 2130538 T3 JP 3830565 B2 JP 8193040 A JP 2006219495 A	15-04-1999 21-08-1996 20-05-1999 05-08-1999 24-07-1996 01-07-1999 04-10-2006 30-07-1996 24-08-2006
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CN 1460549	A	10-12-2003	NONE	
JP 2004074061	A	11-03-2004	NONE	