

COLLOIDAL PALLADIUM-GOLD ALLOY CATALYST FOR VINYL ACETATE PRODUCTION

5 Field of Invention

The present invention relates generally to catalyst preparation and specifically to preparation of a supported catalyst for use in the production of vinyl acetate (VA).

Background of the Invention

10 A well-known commercial process for the production of vinyl acetate is by the gas phase reaction of ethylene, acetic acid and oxygen in the presence of a supported catalyst which contains palladium.

A preferred type of vinyl acetate catalyst is one having a content of palladium metal and gold metal distributed on the surface of a support substrate such as silica or alumina.

15 Numerous methods are known in the art for the production of a supported catalyst for use in the production of VA. A general route employed by the art to prepare a supported catalyst for VA production involves impregnating a support (e.g., alumina or silica) with metal solution, fixing the metals onto the support, and reducing the metal. It has been found that when this general technique is employed for palladium and gold, it frequently yields a catalyst in which
20 palladium and gold are partially or wholly segregated.

Prior art references which describe supported palladium-gold catalysts for vinyl acetate production include United States Patent Numbers 3,761,513; 3,775,342; 3,822,308; 3,939,199; 4,048,096; 4,087,622; 4,133,962; 4,902,832; 5,194,417 5,314,858; and references cited therein; incorporated by reference.

25 The activity and selectivity of a supported palladium-gold catalyst is affected by the physiochemical form of the palladium and gold metal content on the support surface. It is difficult to achieve a uniform microstructure of metal particles by some of the route(s) currently known in the art. The performance of a vinyl acetate manufacturing process is influenced by the uniformity of the palladium-gold catalyst microstructure.

30 In view of the above issues, the art is always searching for new techniques to develop a supported catalyst with improved microstructure, metal distribution, and selectivity for vinyl acetate production.

Summary of the Invention

It is an object of this invention to provide a supported palladium-gold catalyst composition with improved selectivity in vinyl acetate production from ethylene, acetic acid and oxygen.

5 It is another object of this invention to provide a supported vinyl acetate catalyst which has a uniform microstructure of palladium and gold metal on a support substrate.

It is a further object of this invention to provide a process for producing a vinyl acetate catalyst which yields a uniform distribution of a colloidal palladium-gold alloy on a support surface.

10 Other objects and advantages of the present invention shall become apparent from the accompanying description and examples.

The present invention relates generally to preparation of a supported catalyst for use in the production of vinyl acetate. It relates specifically to a process for the preparation of a supported catalyst, and to the catalyst prepared from said process, for production of vinyl acetate from ethylene, acetic acid, and oxygen, which process comprises:

- 1) forming an aqueous solution of water-soluble palladium and gold compounds;
- 2) dispersing the aqueous solution in a hydrophobic solvent with an effective amount of surfactant to form a microemulsion mixture;
- 3) treating the microemulsion mixture with a reducing agent; and,
- 20 4) impregnating a support with the mixture of step (3) to form a supported metal catalyst.

Optionally, the supported catalyst of step (4) may be washed and dried. This inventive preparation differs from the art, in part, to its sequence of preparation. Unlike the art, here, the metals are reduced before the substrate is impregnated. This sequence differential has been found to result in a supported catalyst that has improved efficiency for the production of VA.

Description of the Invention

One or more objects of the present invention are accomplished by a process for the preparation of a catalyst for production of vinyl acetate from ethylene, acetic acid and oxygen, which process comprises

- 30 1) forming an aqueous solution of water-soluble palladium and gold compounds;
- 2) dispersing the aqueous solution in a hydrophobic solvent with an effective amount of surfactant to form a microemulsion mixture;

- 3) treating the microemulsion mixture with a reducing agent; and,
- 4) impregnating a support with the mixture of step (3) to form a supported metal catalyst.

Optionally, the supported catalyst of step (4) may be washed and dried.

5 The term "hydrophobic" as employed herein refers to an organic hydrocarbon solvent which has a water-solubility of less than about one gram per one hundred grams of water at 100 °C.

The term "microemulsion" as employed herein refers to a water-in-oil type of mixture in which the dispersed aqueous phase preferably has an average droplet size less than about five microns.

10 The term "alloy" as employed herein refers to a molecular mixture of at least two different metals. Discussion herein refers to the metals palladium and gold, and the term "alloy" is intended to mean molecular mixtures which are substantially free of segregated palladium and gold.

The terms "support", "support medium", and "substrate" are used herein interchangeably.

15 The inventive process will be described relative to each step. The description illustrates a preferred embodiment of the present invention. Generally it is directed to discussion of palladium and gold on alumina or silica support. It is to be understood by those of skill in the art that this technique is suitable for use with a variety of metal alloys and support substrates. The description herein is not intended to be limited to palladium and gold alloy on alumina or silica
20 substrates. Other support substrates may be employed and will be discussed in further detail below. Unless indicated otherwise, the order of addition of reagents within each step is not crucial to the invention.

Step (1): In the inventive process, the first step involves forming an aqueous solution of water-soluble palladium and gold compounds. Generally the route employed for step (1)
25 involved dissolving the metal salts in water. It is preferred to use water which is deionized or distilled to avoid additional salt impurities. The metal salts, sodium palladium chloride (Na_2PdCl_4) and chloroauric acid ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$), were placed in a round bottom flask with a stir bar and water was added thereto. Stirring was accomplished at room temperature under atmospheric conditions. Stirring may be done under an inert atmosphere if desired.

30 Water is added in as minimum an amount as possible. The quantity of water is minimized to facilitate the formation of a water-in-oil dispersion, in which the water droplets are in a micronized form, i.e., the droplets have an average size of about or less than 5 microns in

diameter. It is preferred to add a sufficient amount of water to the metal salts to form a saturated salt solution. A range consists of about 1:1, (1 g water: 1 g metal salt) to saturation of the metal salt in water. Preferably, the range is about 1:3.

Step (2): Step (2) relates to dispersing the aqueous solution of step (1) in a hydrophobic solvent with an effective amount of surfactant to form a microemulsion mixture.

In the inventive process, between about 0.5-5 milliliters of water are employed per 30 milliliters of microemulsion mixture in step (2) of the process. The micronized dispersion of water-in-oil solution of palladium and gold compounds effectively provides a colloidal dispersion of palladium-gold alloy in the step (3) metal reduction step of the invention process.

Hydrophobic organic solvents suitable for use in step (2) include but are not limited to pentane, hexane, cyclohexane, heptane, octane, iso-octane, naphtha, naphthene, benzene, chlorobenzene, dichloromethane, and the like. Pentane is the preferred solvent.

The preferred amount of hydrophobic solvent is dependent on the pore volume of the support. Preferably a sufficient or effective amount of solvent is employed to saturate the pore volume of the support. It is desirable to avoid an excess of solvent. Routine experimentation to test for absorptivity of the support relative to the solvent will determine the quantity of solvent to employ.

The surfactant ingredient can be selected from a wide range of non-ionic, anionic and cationic products which are commercially available. Illustrative of suitable surfactants are cetyltrimethylammonium bromide; sodium lauryl sulfate; sodium dodecylbenzenesulfonate; ammonium lignosulfonate; condensation products of ethylene oxide with fatty alcohols, amines or alkylphenols; partial esters of fatty acids and hexitol anhydrides; and the like. A non-ionic surfactant is preferred for purposes of the present invention process. Preferred surfactants include pentaethylene glycoldodecyl ether, trioctylphosphine oxide, and Genepol® (commercially available product from Hoechst Celanese Corporation), with the most preferred surfactant being Genepol®.

The surfactant ingredient can be employed in a quantity between about 2-20 grams per 30 milliliters of microemulsion mixture. It was observed that too small an amount of surfactant did not permit formation of a microemulsion. Although no upper limit for an amount of surfactant to employ was detected, an excess of surfactant is wasteful. It is desirable to utilize a sufficient or effective amount of surfactant to form a microemulsion. The amount of surfactant will vary based on the amount of water employed in step (1) and the type of surfactant being used.

Generally, routine laboratory experimentation can determine a satisfactory minimum amount of surfactant to employ.

The order of addition for step 2 generally involved adding solvent to surfactant, followed by mixing (mixing can be accomplished by any conventional means). Generally, the solvent/surfactant mixture was mixed until a homogeneous, pourable, solution was obtained. This pourable mixture was then added to the metal salt solution of step (1) and mixing was continued until a microemulsion was formed. Employing palladium, and gold metal salts, and pentane as solvent, a color change was observed at step (2). The color will vary depending on the metal and solvent employed.

Step (3): Step (3) defines a particularly inventive aspect of the present invention process. In step (3) the microemulsion mixture is treated with an excess quantity of reducing agent, such as hydrazine, ethylene gas, or formaldehyde, to reduce the palladium and gold to the metallic state and form a suspended colloidal alloy phase of palladium and gold metal in the microemulsion mixture.

In accordance with the inventive process, the reduction step is conducted prior to the metal mixture being impregnated on the support. If the reduction step is conducted after the microemulsion mixture is impregnated on the support, the resulting catalyst has been found to have the palladium and gold metal segregated and be less selective for production of vinyl acetate from ethylene, acetic acid and oxygen.

It is highly beneficial, and recommended, to complete the reduction reaction to as near as possible. Generally, when employing hydrazine, or a reducing agent which causes the evolution of gas, the reaction can be monitored based on the evolution of gas, in which case, it is best to continue the reaction until gas ceases to evolve from the reaction.

In the preferred embodiment, hydrazine was added to the microemulsion mixture in a range of about 1 to 2 mls per 3 g of metal salts employed. The resultant reaction was exothermic. The mixture was allowed to cool before proceeding to step (4).

Step (4): Step (4) involves impregnating an inorganic support with the reduced metals-mixture of step (3) to form a supported metal catalyst. Impregnation may be conducted following conventional procedures. The support substrate for the vinyl acetate catalyst can be selected from organic or inorganic support substrates. Due to their stability for the production of VA, inorganic supports are preferred. Suitable inorganic supports include but are not limited to silica, alumina, silica/alumina mixture, zirconium dioxide, titanium dioxide, calcium dioxide,

and the like, as well as other types of solid carriers widely employed for the manufacture of vinyl acetate catalysts. Silica and alumina are the preferred solid carriers to employ for the production of VA, with alumina being the most preferred, and α -alumina being most most preferred.

The vinyl acetate catalyst support medium can be in the form of spheres, tablets, Raschig rings, and the like.

Generally for the present invention, the support medium was used as received with no preparatory treatment. The support was added to the cooled mixture of step (3) under atmospheric conditions and mixed. Mixing occurred manually, however any conventional suitable means is acceptable.

The supported catalyst is impregnated with an activator ingredient such as an alkali metal alkanoate (e.g., potassium acetate, potassium borate), to provide a catalyst product with enhanced selectivity for vinyl acetate production from ethylene, acetic acid and oxygen.

Optional Step (5): Although not a necessary step, the impregnated catalyst support formed during step (4) was repeatedly washed with a co-solvent for water and solvent and surfactant, such as alcohol (ethanol) followed by a water wash. This washing removed any residual hydrophobic solvent, surfactant, and salts from the supported catalyst. If desired, the wash step may be omitted since catalyst residues would burn off in the reactor during use of the supported catalyst. The supported catalyst was then dried in a standard convection oven or fluid bed drier. Drying by conventional means is acceptable. Drying temperatures employed ranged from about 150 °C to about 300 °C under a nitrogen atmosphere. If this step is employed, KOAc impregnation follows.

Discussion of Examples

As demonstrated in the Examples, alumina is a preferred type of support medium.

Although a supported catalyst was prepared utilizing the present technique with silica, it was observed that greater metal retention to substrate was obtained when employing alumina.

In Catalyst Examples 1-3, the palladium-gold supported catalysts have a silica substrate. It was observed that these supported catalysts did not possess as uniform, homogeneous physical appearance, as the catalyst supported on an alumina substrate. It was further observed that the catalyst examples 1-3, with a silica substrate, had insufficient metal loading on the surface to conduct performance testing. This is in contrast to Example 9, which exhibited a high retention of colloidal palladium-gold alloy on the alumina surfaces of the substrate, and exhibited

excellent selectivity for the production of vinyl acetate from ethylene, acetic acid and oxygen.

Supported Catalyst Composition

In addition to providing a process to prepare a supported catalyst, this invention provides
5 a catalyst composition for the preparation of vinyl acetate from ethylene, acetic acid and oxygen, which comprises colloidal palladium-gold alloy on a support medium, preferably on an alumina support. "Colloidal" herein refers to a uniform particle composition on the support with respect to palladium and gold; "Uniform" as compound to supported Pd/Au catalyst produced by prior art support techniques.

10 The colloidal palladium-gold alloy on the alumina support typically has an average particle size between about 1-20 nanometers.

An invention vinyl acetate catalyst on alumina can have a palladium metal content between about 0.1-2.5 weight percent, and a gold metal content between about 0.05-0.6 weight percent based on the catalyst weight.

15 The catalyst palladium-gold weight ratio can vary between about 1-10:1.

A present invention catalyst composition has particular advantage when utilized in the manufacture of vinyl acetate monomer from ethylene, acetic acid and oxygen. A typical vinyl acetate process involves the reaction of ethylene, acetic acid and oxygen or air in the gas phase at about 100 -250 °C and normal or elevated pressure in the presence of a supported catalyst which
20 contains palladium. Various vinyl acetate processing embodiments are described in the references recited in the Background section.

The following examples are further illustrative of the present invention. The components and specific ingredients are presented as being typical, and various modifications can be derived in view of the foregoing disclosure within the scope of the invention.

EXAMPLES

General Procedure for VA Production

When employing a Vinyl Acetate Stirred Tank Reactor (VAST) Unit in the Examples the following general procedure was employed. The VAST is a Berty reactor, or a continuous
30 stirred tank reactor of the recirculating type that is run at constant oxygen conversion (about 45%). The supported catalyst is loaded in a basket in the reactor, a measured amount of acetic acid, ethylene, and oxygen is added in a nitrogen diluent, and the reactor is brought up to

temperature by means of a heating mantle., The temperature in the reactor is measured above and below the catalyst. The reaction is terminated after approximately 18 hours at a temperature at which 45% oxygen conversion is maintained. Products are measured by gas-phase chromatography. CO₂ selectivities tend to be a little higher for the same catalyst when tested in the VAST Unit compared to the VAMU since the product vinyl acetate is recirculated in contact with the catalyst during the reaction sequence.

The Vinyl Acetate Micro Unit (VAMU) reaction in the Examples is a plug flow type reaction system operated at constant temperature. The VAMU reactor is a 3 ft-long, 16 mm i.d. stainless steel tube with a 3 mm concentric thermocouple well. The reactor is equipped with a heating jacket through which hot water and steam are circulated. Generally, a 30 cc sample of catalyst is diluted with support up to 150 cc and loaded to the reactor. The catalyst/support mixture is topped with 30 cc of support. After a single pass-through of the oxygen, ethylene and acetic acid in a nitrogen diluent at constant temperature, the products are analyzed by gas-phase chromatography.

Example 1 (SiO₂ Support Example)

This Example illustrates the preparation of a Pd-Au metal on a silica support type of catalyst by a microemulsion method.

Na₂PdCl₄ (2.26 g, 7.8 mmol) and HAuCl₄•3H₂O (827 mg, 2.1 mmol) were dissolved in 1.6 mL of deionized water under nitrogen in a reaction flask. A solution of Genapol® 26-L-60 (12.5 g, Hoechst Celanese) in pentane (35 mL) was prepared. The two solutions were mixed to form a microemulsion of the aqueous phase in the organic solvent phase. Hydrazine monohydrate (2 mL) reducing agent was added under nitrogen, and the solution turned black and gas evolution was evident.

The reduced solution was applied to Aerosil 200 with MgO binder (Degussa). The formed supported catalyst was shaken for 10 minutes, and purged under nitrogen to remove the pentane solvent. The supported catalyst was washed with ethanol, and then washed with demineralized water for 16 hours. The supported catalyst was dried in a fluidized bed drier for one hour at 100°C, and then dried at 150°C for 20 hours under nitrogen.

The supported catalyst was impregnated with potassium acetate activator (6 g in 50 mL of water), and dried in a fluidized bed drier at 100°C for one hour.

Example 2 (SiO₂ Support Example)

This Example illustrates the preparation of a Pd-Au metal on a silica support type of catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

5	Na ₂ PdCl ₄	2.26 g, 7.8 mmol
	HAuCl ₄ •3H ₂ O	827 mg, 2.1 mmol
	hydrazine monohydrate	2 mL
	Aerosil 300 with	
	Kaolin binder (Degussa)	64.1 g
10	potassium acetate	6.0 g

Example 3 (SiO₂ Support Example)

This Example illustrates the preparation of a Pd-Au metal on a silica support type of catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

15	Na ₂ PdCl ₄	2.26 g, 7.8 mmol
	HAuCl ₄ •3H ₂ O	827 mg, 2.1 mmol
	hydrazine monohydrate	2 mL
	Aerosil 300 with	
20	Al ₂ O ₃ binder (Degussa)	56.6 g
	potassium acetate	5.0 g

Example 4

This Example illustrates the preparation of a present invention type of Pd-Au metal alloy on an alumina support catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

25	Na ₂ PdCl ₄	2.26, 7.8 mmol
	HAuCl ₄ •3H ₂ O	827 mg, 2.1 mmol
30	hydrazine monohydrate	2 mL
	alumina Raschig rings	88.0 g
	potassium acetate	4.0 g

X-ray absorption spectroscopy indicated a distribution of a colloidal Pd-Au alloy having an average particle size in the range of 1-20 nanometers.

The selectivity of the catalyst of example 4 was tested in a stirred tank process (VAST) for the preparation of vinyl acetate from ethylene, acetic acid and oxygen. The comparative data are summarized in Tables I-II.

Example 5 (SiO₂ Support Example)

This Example illustrates the preparation of a Pd-Au metal on a silica support type of catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

Na ₂ PdCl ₄	2.26 g, 7.8 mmol
HAuCl ₄ •3 H ₂ O	827 mg, 2.1 mmol
hydrazine hydrate	2 mL
Süd Chemie T-4358-E-1	59.3 g
potassium acetate	5.0 g

The selectivity of this catalyst was tested in a micro unit (VAMU) for the preparation of vinyl acetate. The comparative data are summarized in Tables II and III.

Example 6 (SiO₂ Support Example)

This Example illustrates the preparation of a Pd-Au metal on a silica support type of catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

Na ₂ PdCl ₄	2.26, 7.8 mmol
HAuCl ₄ •3 H ₂ O	827 mg, 2.1 mmol
hydrazine monohydrate	2 mL
Süd Chemie T-4358-E-1	59.3 g
potassium acetate	5.0 g

The selectivity of this catalyst was tested in a micro unit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and III.

Example 7

This Example illustrates the preparation of a present invention type of Pd-Au metal alloy

on an alumina support catalyst by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

	Na_2PdCl_4	2.35 g, 8 mmol
5	$\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$	788 mg, 2 mmol
	hydrazine monohydrate	1.5 mL
	$-\text{Al}_2\text{O}_3$ tablets (Aesar)	155.0 g
	potassium acetate	5.0 g

The selectivity of this catalyst was tested in a micro unit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and IV.

Example 8

This Example illustrates the preparation of a present invention type of Pd-Au metal alloy on an alumina support by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities. The procedure was repeated to form a double coat of Pd-Au alloy on the alumina support.

	Na_2PdCl_4	2.65 g, 9 mmol
	$\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$	394 mg, 1 mmol
	hydrazine monohydrate	1.5 mL
20	$-\text{Al}_2\text{O}_3$ tablets (Aesar)	155.0 g
	potassium acetate	
	(second coat)	5.0 g

The selectivity of this catalyst was tested in a microunit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and IV.

Example 9

This Example illustrates the preparation of a present invention type of Pd-Au metal alloy on an alumina support by a microemulsion method. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities. The procedure was repeated to form a double coat of Pd-Au alloy on the alumina support.

	Na_2PdCl_4	2.35 g, 8 mmol
	$\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$	788 mg, 2 mmol

hydrazine monohydrate - 1.5 mL

-Al₂O₃ tablets (Aesar) 155.0 g

potassium acetate

The selectivity of this catalyst was tested in a micro unit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and IV.

Example 10

This Example illustrates the preparation of a Pd-Au metal on an alumina support type of catalyst by a microemulsion method, in which the palladium metal and the gold metal are applied in separate coatings. The supported catalyst of this example was prepared in accordance with example 1 employing the following reagents and quantities.

First coating

Na₂PdCl₄ 2.94 g, 10 mmol

hydrazine monohydrate 1.5 mL

-Al₂O₃ tablets (Aesar) 155 g

Second coating

HAuCl₄•3 H₂O 985 mg, 2.5 mmol

hydrazine monohydrate 1.0 mL

potassium acetate 5.0 g

The selectivity of this catalyst was tested in a microunit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and V.

Examples 11-12

These Examples illustrate the preparation of present invention Pd-Au metal alloy on alumina support type of catalysts by a microemulsion method.

Na₂PdCl₄ 4.41 g, 15 mmol

HAuCl₄•3 H₂O 1.97 g, 5 mmol

hydrazine monohydrate 3.0 mL

-Al₂O₃ tablets (Aesar) 310.0 g

potassium acetate 5.0 g

The initial supported catalyst was prepared by a procedure similar to the microemulsion method of Example 1, and then the catalyst product was divided into two 155 g portions.

One portion was dried at 150 °C for 16 hours under nitrogen, and impregnated with potassium acetate (5 g in water), and dried at 100 °C for one hour (Example 11).

The second portion was calcined at 300 °C for 5 hours in air, impregnated with potassium acetate (5 g in water), and dried at 100 °C for one hour (Example 12).

5 The selectivity of these catalysts were tested in a micro unit for the preparation of vinyl acetate. The comparative data are summarized in Tables I and V.

Examples 13-14

10 These Examples illustrate the preparation of Pd-Au metal on alumina support type of catalysts by an incipient wetness method.

-Al₂O₃ Raschig rings were impregnated with a 32 mL aqueous solution containing Na₂PdCl₄ (3.47 g) and NaAuCl₄ (3.47 g). NaOH (1.1 g in 120 mL of H₂O) was added, and the mixture was allowed to stand for 20 hours.

15 The resulting catalyst precursor was washed with demineralized water, and dried. The catalyst then was impregnated again with the same type of Pd-Au solution. The catalyst was dried at 100 °C for one hour, then impregnated with aqueous NaOH (1.1 g in 32 mL of H₂O). After standing for 15 hours, the catalyst was washed with demineralized water for 25 hours, dried at 100 °C for one hour, and then at 150 °C for 24 hours under nitrogen. The catalyst was impregnated with potassium acetate (5 g in 32 mL of H₂O), and dried at 100 °C for one hour
20 (Example 13).

The supported catalyst of Example 14 was prepared following the above described incipient wetness method, with Pd-Au in a 6:1 ratio on α -alumina tablets.

The selectivity of the catalyst of Example 13 was tested in a stirred tank process for the preparation of vinyl acetate. The data are summarized in Table II.

25 The selectivity of the catalyst of Example 14 was tested in a micro unit process for the preparation of vinyl acetate. The comparative data are summarized in Table V.

Comments regarding Tables

30 Selectivity data is reported as being conducted in either VAMU or VAST unit. The supported catalysts were analyzed by X-ray Fluorescence Spectroscopy (XFS) unless otherwise indicated. Shell Temp. is the temperature of the hot water around the plug-flow reactor. Double = means two catalyst coatings were placed on support or substrate.

Abbreviations in Tables:

STY = space-time-yield

ICP = inductively coupled plasma spectroscopy

ADJ O₂ Conv= adjusted oxygen conversion

5

HE = heavy ends

EtOAc = ethyl acetate

HOAc = acetic acid

TEM = transmission electron microscopy

TTL = total

10

AFB = after found bases

TABLE I

Data Of Catalysts Prepared By Microemulsion Process

5	<u>DESCRIPTION</u>	<u>ANALYSIS</u>	
	Example 1, SiO ₂ Aerosil 200/MgO binder BET SA = 186 m ² /g Pore Vol. 0.82 cc/g 4:1 Pd:Au	0.23% Pd, 0.10% Au 75 ppm Cl, 4.9% KOAc	speckled catalyst insufficient metal loading for analysis
10			
	Example 2, SiO ₂ Aerosil 300/kaolin binder BET SA = 245 m ² /g Pore Vol. 0.81 cc/g 4:1 Pd:Au	0.30% Pd, 0.13% Au, <50 ppm Cl, 5.4% KOAc	speckled catalyst insufficient metal loading for analysis
15			
	Example 3, SiO ₂ Aerosil Al ₂ O ₃ binder BET SA = 238 m ² /g Pore Vol. 1.02 cc/g 4:1 Pd:Au	0.30% Pd, 0.13% Au, <50 ppm Cl, 5.3% KOAc	speckled catalyst insufficient metal loading for analysis
20			
	Example 4 α -Al ₂ O ₃ Raschig rings BET SA = 0.7 m ² /g Pore Vol. 0.45 cc/g 3:1 Pd:Au	0.58% Pd, 0.35% Au(ICP)	VAST run 46.9 g catalyst Temp. 173 C CO ₂ selectivity 12%
25			
	Catalyst 5, SiO ₂ Sud Chemie, T-4358-E-1 BET SA = 235 m ² /g Pore Vol. 0.91 cc/g 3:1 Pd:Au	0.86% Pd, 0.52% Au <50 ppm Cl, 5.1% KOAc Post reaction analysis: 0.63% Pd, 0.34% Au 9.1% KOAc	VAMU run 16.2 g catalyst Temp. 179 C O ₂ conv. 31.5% CO ₂ selectivity 10.7%
30			
	Example 6, SiO ₂ Sud Chemie, T-4358-E-1 BET SA = 235 m ² /g Pore Vol. 0.91 cc/g 4:1 Pd:Au	0.53% Pd, 0.25% Au <50 ppm Cl, 7.1% KOAc Post reaction analysis: 0.43% Pd, 0.20% Au, 8.4% KOAc	VAMU run 16.3 g catalyst Temp. 179 C O ₂ conv. 18.8% CO ₂ selectivity 8.5%
35			
	Example 7 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g	0.37% Pd, 0.17% Au (ICP)	VAMU run 35.5 g catalyst Temp. 155 C; 160 C
40			
45			

TABLE I, continued

5	Pore Vol. 0.25 cc/g 4:1 Pd:Au		O ₂ conv. 18.7% 21.1% CO ₂ selective. 7.1% 7.7%
10	Example 8 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g Pore Vol. 0.25 cc/g 7:1 Pd:Au, Double coat	0.80% Pd, 0.21% Au (ICP)	VAMU run 35.5 g catalyst Temp. 145 C; 150 C O ₂ conv. 30.3%, 36.7% CO ₂ selectivity 7.1%, 7.7%
15	Example 9 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g Pore Vol. 0.25 cc/g 4:1 Pd:Au, Double coat	0.502% Pd, 0.24% Au 0.54% K (ICP)	VAMU run 35.1 g catalyst Temp. 151 C O ₂ conv. 35.6% CO ₂ selectivity 7.7%
20	Example 10 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g Pore Vol. 0.25 cc/g Pd coated then Au coated	0.47% Pd, 0.25% Au 0.65% K (ICP)	VAMU run 35.9 g catalyst Temp. 155 C O ₂ conv. 21.31% CO ₂ selectivity 8.39%
25	Example 11 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g Pore Vol. 0.25 cc/g 3.1:1 Pd:Au dry at 150 °C	0.30% Pd, 0.18% Au 0.31% K (ICP)	VAMU run 35.5 g catalyst Temp. 155 C O ₂ conv. 24% CO ₂ selectivity 7.1%
30	Example 12 α -Al ₂ O ₃ tablets BET SA = 4 m ² /g Pore Vol. 0.25 cc/g 3:1 Pd:Au calcined 300 °C	0.28% Pd, 0.17% Au 0.88% K (ICP)	VAMU run 35.5 g catalyst Temp. 155 C O ₂ conv. 23% CO ₂ selectivity 9.0%
35			

TABLE II
(Comparative Table of Data)

Vinyl Acetate Stirred Tank Process. With Pd-Au On α -Alumina Support

5	Example Number	4	8	13
	Catalyst ID	3.1:1Al ₂ O ₃	7:1 Al ₂ O ₃	2.2:1 Al ₂ O ₃
	Catalyst Age, Hrs.	18.00	20.000	19.500
	Sel. to CO ₂ (a,b)	11.984	12.285	11.152
10	Sel. to HE	0.504	0.569	0.614
	Sel. to ETOAC	0.068	0.144	0.063
	STY g VA/L/Hr (a,c)	675.754	544.238	695.656
	ADJ O ₂ Conv. (d)	45.755	45.224	46.575
	Reactor Top Deg. C (e)	172.800	156.300	164.270
15	Reactor Bot Deg. C (e)	175.500	160.800	167.230
	Pressure.PSIG	170.100	170.000	169.840
	O ₂ Feed, moles/hr	1.017	1.020	1.016
	C ₂ H ₄ Feed, moles /hr	5.007	5.007	5.000
	HOAC Feed, moles /hr	1.976	1.908	1.937
20	N ₂ FEED, moles /hr	4.942	4.942	4.940
	O ₂ Account.% (f)	96.802	94.645	96.643
	C ₂ H ₄ Account.% (g)	99.083	98.057	99.152
	HOAC Account.%(h)	101.118	99.994	106.462
	Mass Account.%(i)	99.711	98.897	101.156
25	wt% Pd (ICP)	0.58%	0.80%	1.1%
	wt% Au	0.35%	0.21%	0.89%
	MeanTEM Particle Size(k)	10.7 nm		8.3 nm

Notes:

- 30 (a) Normalized to 45% O₂ conversion.
- (b) Adj. CO₂ Sel = (moles CO₂ product minus moles CO₂ fed)100/2 (adj. C₂H₄ conv.), where
adj. C₂H₄ conv. = moles C₂H₄ accounted for minus moles C₂H₄ product.
- (c) STY, g VA/1-hr = (VA produced, g/hr x 1000)/catalyst volume, ml.
- 35 (d) Adj. O₂ Conv. = (moles O₂ fed, AFB minus moles O₂ product)100/moles O₂ fed, where
AFB = accounted for basis.
- (e) The reactor temperature, degrees C, is the average of the circulation gas temperature above
and below the catalyst.
- (f) O₂ Account. = (total moles O₂ recovered, AFB/total moles O₂ fed)100.
- (g) C₂H₄ Account. = (total moles C₂H₄ recovered, AFB/total moles C₂H₄ fed)100.
- 40 (h) HOAc Account. = (total moles HOAc recovered, AFB/total moles HOAc fed)100.
- (i) Mass Account. = (total grams product recovered/total grams fed)100.
- (k) TEM measurement performed after run in VAST unit.

TABLE III

Vinyl Acetate Micro Unit Process, With Pd-Au On Silica Support

5	Example Number	5	6
	Catalyst ID	3:1 Pd/Au metal on T-4358-E-1	4:1 Pd/Au metal on T-4358-E-1
	Size	5 mm	5 mm
10	Avg. Cat. Temp.	178.800	179.520
	Shell Temp.	173.900	177.650
	Pressure	100.000	100.000
	O ₂ /N ₂ Rate (cc/min)	896.840	897.290
	C ₂ H ₄ Rate (cc/min)	1014.070	1014.580
15	HOAc Rate (mL/min)	0.800	0.800
	STY (g/L/hr)	352.024	262.756
	Mass Acct. (%)	100.001	99.826
	O ₂ Conv. (%)	31.502	18.776
	C ₂ H ₄ Conv. (%)	13.395	10.630
20	AcOH Conv. (%)	7.129	5.367
	O ₂ Acct. (%)	101.141	103.298
	C ₂ H ₄ Acct. (%)	98.466	98.709
	AcOH Acct. (%)	101.370	100.390
	VA Sel. (%)	88.751	90.911
25	CO ₂ Sel. (%)	10.745	8.555
	EtOAc Sel. (%)	0.126	0.130
	TTL HE Sel. (%)	0.379	0.403
	Selectivity values are normalized and based on ethylene.		

TABLE IV

Vinyl Acetate Micro Unit Process. With Pd-Au On α -Alumina Support

5	Example Number	7	7	8	8	9
	Catalyst ID	4:1 alloyed-Pd/Au on Al ₂ O ₃	4:1 alloyed-Pd/Au on Al ₂ O ₃	7:1 alloyed-Pd/Au on Al ₂ O ₃	7:1 alloyed-Pd/Au on Al ₂ O ₃	4:1 alloyed-Pd/Au on Al ₂ O ₃
	no. coats			Double	Double	Double
10	Size	3 mm	3 mm	3 mm	3 mm	3 mm
	Avg. Cat. Temp.	157.130	162.130	147.730	152.930	154.520
	Shell Temp.	155.450	160.500	145.650	149.950	151.050
	Pressure	100.000	100.000	100.000	100.000	100.000
	O ₂ /N ₂ (15/85) Rate (cc/min)	902.000	894.210	904.530	905.070	928.700
15	C ₂ H ₄ Rate (cc/min)	1015.090	1006.320	1023.700	1024.310	1056.420
	HOAC Rate (mL/min)	0.810	0.820	0.820	0.820	0.800
20	STY (g/L/hr)	251.442	309.747	417.847	492.272	435.261
	Mass Acct. (%)	99.658	100.308	100.696	100.855	98.248
	O ₂ Conv. (%)	18.174	21.118	30.353	36.754	35.648
	C ₂ H ₄ Conv. (%)	8.973	8.979	13.667	14.892	20.508
	AcOH Conv. (%)	6.364	7.564	7.685	9.858	9.820
25	O ₂ Acct. (%)	101.807	104.459	102.739	103.375	98.985
	C ₂ H ₄ Acct. (%)	97.489	97.252	98.648	97.646	96.631
	AcOH Acct. (%)	101.522	103.767	103.485	105.289	97.886
	VA Sel.	91.952	91.416	92.185	91.617	91.361
	CO ₂ Sel.	7.081	7.738	7.098	7.735	7.713
30	EtOAc Sel.	0.149	0.132	0.198	0.186	0.175
	Total HE Sel.	0.817	0.714	0.518	0.462	0.751
	wt. % Pd	0.37	0.37	0.80	0.80	0.50
	wt. % Au	0.17	0.17	0.21	0.21	0.24

TABLE V

Vinyl Acetate Micro Unit Process With Pd-Au On α -Alumina Support

5	Example Number	10	11	12	13	14
	Catalyst ID	Pd coat then Au coat on Al_2O_3	3:1 Pd/Au	3:1 Pd/Au	3:1 Pd/Au	6:1 Pd/Au incipient wetness
10	Size	3 mm	3 mm	3 mm	3 mm	3 mm
	Avg. Cat. Temp.	157.500	157.920	156.620	167.800	159.370
	Shell Temp.	155.750	155.350	153.610	163.800	156.050
	Pressure	100.000	100.000	100.000	100.000	100.000
15	O_2/N_2 (15/85) Rate (cc/min)	918.860	913.090	903.530	907.510	915.180
	C_2H_4 Rate (cc/min)	1045.230	1038.670	1021.430	1030.460	1038.180
	HOAc Rate (mL/min)	0.790	0.800	0.850	0.800	0.800
20	STY (g/L/hr)	236.543	321.512	279.441	375.372	443.986
	Mass. Acct. (%)	98.350	99.232	99.539	99.378	99.253
	O_2 Conv. (%)	21.311	23.811	23.402	34.379	35.950
	C_2H_4 Conv. (%)	11.611	13.351	9.962	14.937	19.988
25	AcOH Conv.	6.785	7.520	6.942	8.417	8.383
	O_2 Acct. (%)	97.799	101.512	100.641	99.206	101.523
	C_2H_4 Acct. (%)	96.788	97.295	97.397	97.447	98.371
	AcOH Acct. (%)	98.517	100.213	101.125	100.856	98.664
	VA Sel.	90.600	91.967	90.183	88.868	90.570
30	CO_2 Sel.	8.395	7.169	9.046	10.458	8.778
	EtOAc Sel.	0.212	0.192	0.144	0.128	0.224
	Total HE Sel.	0.793	0.672	0.627	0.546	0.429
	wt. % Pd	0.47	0.30	0.28	0.28	0.36
35	wt. % Au	0.25	0.18	0.17	0.17	0.11



CLAIMS

1. A process for the preparation of a catalyst for production of vinyl acetate from ethylene, acetic acid and oxygen, which process comprises

- 5 1) forming an aqueous solution of water-soluble palladium and gold compounds;
2) dispersing the aqueous solution in a hydrophobic solvent with an effective amount of surfactant to form a microemulsion mixture;
3) treating the microemulsion mixture with a reducing agent; and,
4) impregnating a support with the mixture of step (3) to form a supported metal catalyst; and,
10 optionally, washing and drying the supported catalyst of step (4).

2. The process in accordance with claim 1 wherein the hydrophobic organic solvent is a organic hydrocarbon medium.

3. The process in accordance with claim 1 wherein the quantity of surfactant ingredient is between about 2-20 grams per 30 milliliters of microemulsion mixture.

15 4. The process in accordance with claim 1 wherein the surfactant ingredient is a nonionic surfactant.

5. The process in accordance with claim 1 wherein the reducing agent is hydrazine.

6. The process in accordance with claim 1 wherein the support is an inorganic support.

20 7. The process in accordance with claim 6 wherein the support is selected from the group consisting of silica, alumina, silica/alumina mixture, zirconium dioxide, titanium dioxide, and calcium dioxide.

8. The process in accordance with claim 7 wherein the support is alumina.

9. The process in accordance with claim 6 wherein the support is in the form of spherical structures.

25 10. The process in accordance with claim 6 wherein the support medium is in the form of tablets.

11. The process in accordance with claim 6 wherein the support medium is in the form of Raschig rings.

30 12. The process in accordance with claim 7 wherein the alumina catalyst support is α -alumina.

13. The process in accordance with claim 1 wherein the supported metal catalyst of step (4) has a palladium metal content between about 0.1-2.5 weight percent, and a gold metal content

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between about 0.05-0.6 weight percent, based on the catalyst weight.

14. The process in accordance with claim 1 wherein the supported metal catalyst of step (4) has a palladium:gold weight ratio between about 1-10:1.

5 15. The process in accordance with claim 1 further comprising the step of impregnating the supported metal catalyst of step (4) with an aqueous solution of an alkali metal alkanoate activator, and then drying the resultant catalyst.

16. The process in accordance with claim 15 wherein the activator additive is alkali metal acetate.

10 17. A catalyst composition for the preparation of vinyl acetate from ethylene, acetic acid and oxygen, which comprises colloidal palladium-gold alloy on a support medium.

18. The catalyst composition in accordance with claim 17 wherein the colloidal palladium-gold alloy on the support has an average particle size between about 1-20 nanometers.

15 19. The catalyst composition in accordance with claim 17 which has a palladium metal content between about 0.1-2.5 weight percent, and a gold metal content between about 0.05-0.6 weight percent, based on the catalyst weight.

20. The catalyst composition in accordance with claim 17 which has a palladium:gold weight ratio between about 1-10:1.

21. The catalyst composition in accordance with claim 17 which has a palladium content between about 0.1-2 weight percent, based on the catalyst weight.

20 22. The catalyst composition in accordance with claim 17 wherein the support medium is alumina in the form of spherical structures.

23. The catalyst composition in accordance with claim 17 wherein the support medium is alumina in the form of tablets.

25 24. The catalyst composition in accordance with claim 17 wherein the support medium is alumina in the form of Raschig rings.

25. The catalyst composition in accordance with claim 17 wherein the support medium is α -alumina.

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