carboxylic acid esters can be used. Hydrogen, ethylene, propylene, alkaline hydrazine, and alkaline formaldehyde are highly useful reducing agents; and ethylene and hydrogen are particularly preferred. While pure hydrogen may be used, it is more common to use a mixture of hydrogen and an inert gas such as nitrogen, helium, argon, or the like. These mixtures generally contain up to about 50 volume percent (vol.%) hydrogen and, more typically, are comprised of about 5 to 25 vol.% hydrogen and 75 to 95 vol.% inert gas. Reduction times typically vary from 0.1 to 5 h. Temperatures employed for the reduction can range from 20 to 600°C.

The catalyst may be used for the acetoxylation of an olefin, such as ethylene or propylene, to produce an acetoxylated olefin such as vinyl acetate or allyl acetate. Preferably, a promoted catalyst, which can be produced by adding an activator to the reduced catalyst, is used in the acetoxylation reaction. An activator is an alkali or alkaline earth metal compound, examples of which are hydroxides, acetates, nitrates, carbonates, and bicarbonates of potassium, sodium, cesium, magnesium, barium, and the like. Potassium salts are preferred activators. The activator content may be in the range of 0.1 to 15 wt%, preferably 0.5 to 10 wt% of the catalyst.

The invention also includes a process for preparing vinyl acetate, comprising reacting a feed comprising ethylene, oxygen, and acetic acid in the presence of the catalyst.

The feed typically comprises 20 to 70 mol% ethylene, 2 to 8 mol% oxygen, and 2 to 20 mol% acetic acid. The feed may comprise a diluent. Examples of suitable diluents include propane, nitrogen, helium, argon, carbon dioxide, the like, and mixtures thereof.

The reaction is generally performed in a fixed bed reactor at a temperature in the range of 100 to 250°C, preferably 125 to 200°C and under a pressure of ~~15 to 500 psig.~~

EXAMPLE 1

Extrudate Preparation and Characterization:

D-T51 titania (178.2 g), alumina (DISPERAL® P2, available from Sasol, 1.8 g), a high-purity WALOCEL™ C sodium carboxymethyl cellulose (The Dow Chemical Company, 3.8 g), poly(ethylene oxide) (MW = 100,000, 3.4 g), and a cellulose derivative (METHOCEL™ K4M from The Dow Chemical Company, 1.8 g) are mixed for 5 min. Water (100 g), an aqueous ammonium hydroxide (14.8 M, 10.5 g), and benzyl alcohol (1.3 g) are added into the mixture and further mixed to produce a paste. The paste is placed in the hopper of a Bonnot ~~1-inch~~ extruder (The Bonnot Company) equipped with a die face of 2 holes with a diameter of ~~1/8-inch.~~

The extrudates are collected and dried in air at 80°C for 12 h, then calcined in air. The calcination temperature is raised from room temperature to 500°C at a rate of 2°C/min, held at 500°C for 2 h, raised from 500°C to 700°C at a rate of 10°C/min, held at 700°C for 3 h, then lowered to room temperature.

Pd-Au Catalyst:

$NaHCO_3$ powder (2.7 g) is slowly added to an aqueous solution containing $Na_2PdCl_4 \cdot 3H_2O$ (3.1 g), $NaAuCl_4 \cdot 2H_2O$ (1.1 g), and water (23.5 g). The mixture is stirred at room temperature for 10 min. The solution is sprayed with a pipette on the calcined extrudates (100 g) while they are being tumbled in a rotating flask. Once the impregnation is finished, the rotating flask is heated to about 100°C with a heat gun. The impregnated extrudates are tumbled for another 30 min at 100°C, then placed in an oven at 80°C for 2 h before they are cooled to room temperature.

The dried extrudates are washed with warm water (50 to 80°C) until no chloride can be detected by mixing the wash filtrate solution with a 1 wt% silver nitrate solution to observe precipitation. After washing is finished, the catalyst is dried at 80 to 100°C to remove water. Then they are heated at 230°C for 3 h in air, and at 230°C for 30 min under a nitrogen flow. The temperature is raised to 500°C under a flow of 10 mol% hydrogen in nitrogen gas, and held for 3 h before it is cooled to room temperature.

The extrudates are washed with an aqueous solution containing 10 wt% potassium acetate and 1 wt% potassium hydroxide (1 L). The washed extrudates

are dried under nitrogen at 125°C for 2 h. A palladium-gold catalyst is obtained. It contains 0.93 wt% Pd, 0.54 wt% Au, and 1.5 wt% K.

Some physical properties of the catalyst are listed in Table 1. The crush strength of the catalyst is measured with a Chatillon crush strength analyzer (Model DPP 50). The force necessary for failure in 25 measurements of ~~1/8 inch~~ long extrudates is averaged to give the reported value. Bulk density is measured by placing 40 g of the catalyst in a 100-mL graduated cylinder (1" nominal outer diameter). The graduated cylinder is tapped until the apparent volume no longer changes, and then this value is divided into the mass to calculate the bulk density. Voidage is determined by adding the pellets to 50 mL water in a second graduated cylinder and then tapping until all voids are filled. The resulting water level is subtracted from the total volume of the water and the pellets taken separately to determine the void volume occupied by water. Total pore volume is determined by pouring the mixture through a sieve basket, shaking to remove excess water and then weighing the wet extrudates. The increase in mass over the initial 40 g of the catalyst divided by the density of water is taken as the measure of the pore volume.

Vinyl Acetate Production:

The palladium-gold catalyst is tested for vinyl acetate production in a fixed-bed reactor (stainless steel, ~~1 inch~~ O.D.). The reactor is charged with a mixture of the catalyst (10 g) and an inert alpha alumina cylindrical pellets (1/8" in diameter, surface area 4 $m^2/g$, pore volume 0.25 mL/g, 25 g). The feed contains 46.1 mol% helium, 33.9 mol% ethylene, 11.48 mol% acetic acid, 4.2 mol% oxygen, and 4.2 mol% nitrogen. The reactor pressure is ~~80 psig~~ and the space velocity relative to the volume of the catalyst is 3050 $h^{-1}$ at standard temperature and pressure. The reactor is cooled using a fluidized sand bath, the temperature of which is set at 130°C. The product stream is analyzed by gas chromatography (GC). Oxygen conversion, oxygen selectivity, oxygen yield to vinyl acetate, and ethylene selectivity to vinyl acetate between 40 to 50 h on stream are calculated from the GC results and listed in Table 1. Oxygen conversion is calculated by dividing the amount of oxygen consumed by the total amount of oxygen fed to the reactor. Oxygen selectivity to vinyl acetate is the amount of oxygen consumed in making vinyl acetate divided by the total amount of oxygen consumed. Oxygen yield to vinyl acetate is

Table 1

| Example | 1 | 2 | C. 3 | C. 4 |
|---|---|---|---|---|
| Extrudate formulation | | | | |
| DT-51 titania (g) | 178.2 | 162.0 | 144.0 | 180.0 |
| DISPERAL® P2 alumina (g) | 1.8 | 18.0 | 36.0 | 0 |
| Extrudate composition | | | | |
| Titania (wt%) | 99 | 90 | 80 | 100 |
| Alumina (wt%) | 1 | 10 | 20 | 0 |
| Catalyst characterization | | | | |
| Crush strength ~~(lb per 1/8 inch)~~ | ~~10.0~~ | ~~19.3~~ | ~~25.1~~ | ~~5.5~~ |
| Porosity (mL per 100 g) | 45.4 | 47.4 | 45.8 | 47.8 |
| Surface area ($m^2/g$) | 48 | 61 | 101 | 35 |
| Catalyst performance | | | | |
| Oxygen conversion (%) | 71.8 | 67.8 | 53.4 | 66.2 |
| Oxygen selectivity to vinyl acetate (%) | 84.1 | 84.5 | 85.6 | 84.9 |
| Oxygen yield to vinyl acetate (%) | 60.4 | 57.3 | 45.7 | 56.2 |
| Ethylene selectivity to vinyl acetate (%) | 96.9 | 96.9 | 97.2 | 97.1 |
| Catalyst productivity ($g \cdot L^{-1} \cdot h^{-1}$) | 498.7 | 473.1 | 377.3 | 464.0 |

carboxylic acid esters can be used. Hydrogen, ethylene, propylene, alkaline hydrazine, and alkaline formaldehyde are highly useful reducing agents; and ethylene and hydrogen are particularly preferred. While pure hydrogen may be used, it is more common to use a mixture of hydrogen and an inert gas such as nitrogen, helium, argon, or the like. These mixtures generally contain up to about 50 volume percent (vol.%) hydrogen and, more typically, are comprised of about 5 to 25 vol.% hydrogen and 75 to 95 vol.% inert gas. Reduction times typically vary from 0.1 to 5 h. Temperatures employed for the reduction can range from 20 to 600°C.

The catalyst may be used for the acetoxylation of an olefin, such as ethylene or propylene, to produce an acetoxylated olefin such as vinyl acetate or allyl acetate. Preferably, a promoted catalyst, which can be produced by adding an activator to the reduced catalyst, is used in the acetoxylation reaction. An activator is an alkali or alkaline earth metal compound, examples of which are hydroxides, acetates, nitrates, carbonates, and bicarbonates of potassium, sodium, cesium, magnesium, barium, and the like. Potassium salts are preferred activators. The activator content may be in the range of 0.1 to 15 wt%, preferably 0.5 to 10 wt% of the catalyst.

The invention is a process for preparing vinyl acetate, comprising reacting a feed comprising ethylene, oxygen, and acetic acid in the presence of the catalyst.

The feed typically comprises 20 to 70 mol% ethylene, 2 to 8 mol% oxygen, and 2 to 20 mol% acetic acid. The feed may comprise a diluent. Examples of suitable diluents include propane, nitrogen, helium, argon, carbon dioxide, the like, and mixtures thereof.

The reaction is generally performed in a fixed bed reactor at a temperature in the range of 100 to 250°C, preferably 125 to 200°C and under a pressure of (15 to 500 psig) 0.201 to 3.551 MPa.

EXAMPLE 1

Extrudate Preparation and Characterization:

D-T51 titania (178.2 g), alumina (DISPERAL® P2, available from Sasol, 1.8 g), a high-purity WALOCEL™ C sodium carboxymethyl cellulose (The Dow Chemical Company, 3.8 g), poly(ethylene oxide) (MW = 100,000, 3.4 g), and a cellulose derivative (METHOCEL™ K4M from The Dow Chemical Company, 1.8 g) are mixed for 5 min. Water (100 g), an aqueous ammonium hydroxide (14.8 M, 10.5 g), and benzyl alcohol (1.3 g) are added into the mixture and further mixed to produce a paste. The paste is placed in the hopper of a Bonnot (1-inch) 2.54 cm extruder (The Bonnot Company) equipped with a die face of 2 holes with a diameter of (1/8 inch) 3.18 mm.

The extrudates are collected and dried in air at 80°C for 12 h, then calcined in air. The calcination temperature is raised from room temperature to 500°C at a rate of 2°C/min, held at 500°C for 2 h, raised from 500°C to 700°C at a rate of 10°C/min, held at 700°C for 3 h, then lowered to room temperature.

Pd-Au Catalyst:

$NaHCO_3$ powder (2.7 g) is slowly added to an aqueous solution containing $Na_2PdCl_4 \cdot 3H_2O$ (3.1 g), $NaAuCl_4 \cdot 2H_2O$ (1.1 g), and water (23.5 g). The mixture is stirred at room temperature for 10 min. The solution is sprayed with a pipette on the calcined extrudates (100 g) while they are being tumbled in a rotating flask. Once the impregnation is finished, the rotating flask is heated to about 100°C with a heat gun. The impregnated extrudates are tumbled for another 30 min at 100°C, then placed in an oven at 80°C for 2 h before they are cooled to room temperature.

The dried extrudates are washed with warm water (50 to 80°C) until no chloride can be detected by mixing the wash filtrate solution with a 1 wt% silver nitrate solution to observe precipitation. After washing is finished, the catalyst is dried at 80 to 100°C to remove water. Then they are heated at 230°C for 3 h in air, and at 230°C for 30 min under a nitrogen flow. The temperature is raised to 500°C under a flow of 10 mol% hydrogen in nitrogen gas, and held for 3 h before it is cooled to room temperature.

The extrudates are washed with an aqueous solution containing 10 wt% potassium acetate and 1 wt% potassium hydroxide (1 L). The washed extrudates

are dried under nitrogen at 125°C for 2 h. A palladium-gold catalyst is obtained. It contains 0.93 wt% Pd, 0.54 wt% Au, and 1.5 wt% K.

Some physical properties of the catalyst are listed in Table 1. The crush strength of the catalyst is measured with a Chatillon crush strength analyzer (Model DPP 50). The force necessary for failure in 25 measurements of (1/8 inch) 3.18 mm long extrudates is averaged to give the reported value. Bulk density is measured by placing 40 g of the catalyst in a 100-mL graduated cylinder (1" nominal outer diameter). The graduated cylinder is tapped until the apparent volume no longer changes, and then this value is divided into the mass to calculate the bulk density. Voidage is determined by adding the pellets to 50 mL water in a second graduated cylinder and then tapping until all voids are filled. The resulting water level is subtracted from the total volume of the water and the pellets taken separately to determine the void volume occupied by water. Total pore volume is determined by pouring the mixture through a sieve basket, shaking to remove excess water and then weighing the wet extrudates. The increase in mass over the initial 40 g of the catalyst divided by the density of water is taken as the measure of the pore volume.

Vinyl Acetate Production:

The palladium-gold catalyst is tested for vinyl acetate production in a fixed-bed reactor (stainless steel, (1 inch) 25.4 mm O.D.). The reactor is charged with a mixture of the catalyst (10 g) and an inert alpha alumina cylindrical pellets (1/8" in diameter, surface area 4 $m^2/g$, pore volume 0.25 mL/g, 25 g). The feed contains 46.1 mol% helium, 33.9 mol% ethylene, 11.48 mol% acetic acid, 4.2 mol% oxygen, and 4.2 mol% nitrogen. The reactor pressure is (80 psig) 0.651 MPa and the space velocity relative to the volume of the catalyst is 3050 $h^{-1}$ at standard temperature and pressure. The reactor is cooled using a fluidized sand bath, the temperature of which is set at 130°C. The product stream is analyzed by gas chromatography (GC). Oxygen conversion, oxygen selectivity, oxygen yield to vinyl acetate, and ethylene selectivity to vinyl acetate between 40 to 50 h on stream are calculated from the GC results and listed in Table 1. Oxygen conversion is calculated by dividing the amount of oxygen consumed by the total amount of oxygen fed to the reactor. Oxygen selectivity to vinyl acetate is the amount of oxygen consumed in making vinyl acetate divided by the total amount of oxygen consumed. Oxygen yield to vinyl acetate is

**Table 1**

| **Example** | **1** | **2** | **C. 3** | **C. 4** |
|---|---|---|---|---|
| **Extrudate formulation** | | | | |
| DT-51 titania (g) | 178.2 | 162.0 | 144.0 | 180.0 |
| DISPERAL® P2 alumina (g) | 1.8 | 18.0 | 36.0 | 0 |
| **Extrudate composition** | | | | |
| Titania (wt%) | 99 | 90 | 80 | 100 |
| Alumina (wt%) | 1 | 10 | 20 | 0 |
| **Catalyst characterization** | | | | |
| Crush strength kg per mm (lb per 1/8 inch) | (10.0) 1.43 | (19.3) 2.76 | (25.1) 3.58 | (5.5) 0.78 |
| Porosity (mL per 100 g) | 45.4 | 47.4 | 45.8 | 47.8 |
| Surface area ($m^2/g$) | 48 | 61 | 101 | 35 |
| **Catalyst performance** | | | | |
| Oxygen conversion (%) | 71.8 | 67.8 | 53.4 | 66.2 |
| Oxygen selectivity to vinyl acetate (%) | 84.1 | 84.5 | 85.6 | 84.9 |
| Oxygen yield to vinyl acetate (%) | 60.4 | 57.3 | 45.7 | 56.2 |
| Ethylene selectivity to vinyl acetate (%) | 96.9 | 96.9 | 97.2 | 97.1 |
| Catalyst productivity ($g \cdot L^{-1} \cdot h^{-1}$) | 498.7 | 473.1 | 377.3 | 464.0 |

11. A process for preparing vinyl acetate comprising reacting ethylene, oxygen, and acetic acid in the presence of the catalyst of claim 1 .
12. The process of claim 11 wherein the extrudate comprises 0.2 to 10 wt% alumina.
13. The process of claim 11 wherein the extrudate comprises 0.5 to 5 wt% alumina.
14. The process of claim 1 1 wherein the catalyst of claim 1 further comprises a Group 11 metal.
15. The process of claim 14 wherein the Group 11 metal is gold.