



166166



G00002

**CATALYST AND USE THEREOF IN THE PRODUCTION OF VINYL
ACETATE**

The present invention relates to a process for the production of vinyl acetate and to a novel catalyst for use in the process.

Vinyl acetate is generally prepared commercially by contacting acetic acid and ethylene with molecular oxygen in the presence of a catalyst active for the
5 production of vinyl acetate.

The catalyst suitable for use in the production of vinyl acetate may comprise a Group VIII metal, for example palladium, an alkali metal acetate promoter, for example sodium or potassium acetate, and an optional co-promoter, for example cadmium acetate or gold. In particular US 5185308 discloses a
10 process for preparing vinyl acetate by the catalytic oxidation of ethylene in the presence of acetic acid. The catalyst used is a supported palladium catalyst promoted with gold and potassium acetate.

Acetic acid, useful as a feedstock for the production of vinyl acetate, may be prepared by several methods as commonly practiced in the industry, for example
15 by the liquid phase carbonylation of methanol and/or a reactive derivative thereof in the presence of a Group VIII noble metal catalyst, an alkyl iodide promoter and a finite concentration of water. The acetic acid produced is then used as a reactant in the production of vinyl acetate. The process, thus tends to be a two stage process.

20 US 3373189 relates to a process for the production of vinyl acetate from ethylene and oxygen using a palladium catalyst. US 4188490 discloses a process for the production of acetic acid and vinyl acetate using a palladium catalyst on a zinc oxide support. US 3637818 discloses a process for the production of acetaldehyde, acetic acid and vinyl acetate by the oxidation of ethylene in the
25 presence of a noble metal and manganese or cobalt oxides. The aforementioned

processes are carried out in the liquid phase.

We have now found that vinyl acetate can be produced directly from a reactant mixture comprising ethylene, optionally water, and an oxygen-containing gas without the need to initially produce acetic acid as a separate stage in the overall process. Through the use of a modified palladium catalyst, vinyl acetate can be produced directly in a one stage process.

Accordingly, the present invention provides a process for the production of vinyl acetate which comprises reacting ethylene with an oxygen-containing gas, and optionally water, in the presence of a catalyst comprising (1) a catalyst support, (2) palladium, (3) an acid, (4) at least one acetic acid catalyst promoter and (5) at least one vinyl acetate catalyst promoter and/or co-promoter.

In a further embodiment of the present invention there is provided a catalyst for use in the production of vinyl acetate which comprises (1) a catalyst support, (2) palladium, (3) an acid, (4) at least one acetic acid catalyst promoter and (5) at least one vinyl acetate catalyst promoter and/or co-promoter.

The present invention provides a novel and cost effective route for the production of vinyl acetate. The process is not only highly selective towards the production of vinyl acetate but does not require the independent and separate production of acetic acid which is then used as a co-reactant in the process. In contrast, use of the modified palladium catalyst results in the in-situ oxidation of the reactants to produce acetic acid which is then oxidised with ethylene to vinyl acetate. The bi-functional nature of the catalyst results in a direct process.

The present invention provides a process for the production of vinyl acetate from ethylene, an oxygen-containing gas and optionally water. The ethylene may be substantially pure or may be admixed with one or more of nitrogen, methane, ethane, carbon dioxide, hydrogen, and low levels of C₃/C₄ alkenes or alkanes.

The oxygen-containing gas may be air or a gas richer or poorer in molecular oxygen than air. Suitably, the gas may be oxygen diluted with a suitable diluent, for example nitrogen or carbon dioxide. Preferably, the oxygen-containing gas is oxygen.

Water may be optionally co-fed into the reaction chamber. Where water is present in the reaction chamber, it may be present in an amount up to 50 volume percent, preferably in the range from 10 to 30 volume percent.

A small amount of acetic acid may also be introduced into the reaction chamber. Suitably, the acetic acid may be introduced through a recycle stream.

Where it is desired to introduce acetic acid, this may be present in an amount up to 50 volume percent, preferably in the range from 5 to 20 volume percent.

The catalyst of the present invention comprises palladium. The palladium concentration may be greater than 0.5% by weight, preferably greater than 1% by weight based upon the total weight of the catalyst. The palladium concentration may be as high as 10% by weight for fixed bed or fluid bed applications.

The catalyst of the present invention is a supported catalyst. Suitable catalyst supports may comprise porous silica, alumina, silica/alumina, titania, zirconia or carbon. Preferably, the support is silica. Suitably, the support may have a pore volume from 0.2 to 3.5 ml per gram of support, a surface area of 5 to 800 m² per gram of support and an apparent bulk density of 0.3 to 1.5 g/ml. For catalysts used in fixed bed processes, the support typically has dimensions of 3 to 9mm and may be spheric, tablet, extrudate, pill shaped or any suitable shape. For catalysts used in fluid bed processes, the support typically may have a particle size distribution such that at least 60% of the catalyst particles have a particle diameter of below 200 microns, preferably at least 50% less than 105 microns and no more than 40% of the catalyst particles have a diameter of less than 40 microns.

The catalyst composition comprises at least one acetic acid catalyst promoter. Suitable promoters include selenium, titanium, tellurium and/or vanadium-containing compounds. Preferably, the acetic acid catalyst promoter is an oxide, acetate or acetylacetonate of at least one of the aforementioned metals. Preferably, the acetic acid catalyst promoter content of the final catalyst is up to 10% by weight.

In addition to the palladium compound and the acetic acid promoter, the catalyst comprises at least one vinyl acetate catalyst promoter and/or co-promoter, preferably both a promoter and a co-promoter. Suitable promoters include gold, copper and/or nickel, and cadmium acetate. A preferred promoter is gold. Suitable sources of gold include gold chloride, tetrachloroauric acid H₂AuCl₄, NaAuCl₄, KAuCl₄, dimethyl gold acetate, barium acetoaurate or gold acetate. The preferred gold compound is H₂AuCl₄. The metal may be present in an amount of from 0.1 to 10% by weight in the finished catalyst. Suitable co-promoters include alkali or alkaline earth metal salts, preferably an acetate salt, such as potassium or sodium acetate. Preferably, the co-promoter content in the final catalyst is in the range from 0.1 to 9.5% by weight as acetate. A preferred catalyst component (5) is gold and either sodium or potassium acetate.

The catalyst composition comprises an acid. Preferably, the acid is a strong acid. Suitable acids comprise heteropolyacids which may include silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, tungstomolybdophosphoric acid, tungstomolybdosilicic acid,

5 tungstovanadophosphoric acid, tungstovanadosilicic acid, molybdovanadophosphoric acid, molybdovanadosilicic acid, borotungstic acid, boromolybdic acid, tungstomolybdoboric acid, molybdoaluminic acid, tungstoaluminic acid, molybdotungstoaluminic acid, molybdogermanic acid, tungstogermanic acid, molybdotungstogermanic acid, molybdotitanic acid,

10 tungstotitanic acid, molybdotungstotitanic acid, cericmolybdic acid, cerictungstic acid, cericmolybdotungstic acid, molybdocobalt acid, tungstocobalt acid, molybdotungstocobalt acid, phosphoniobic acid, siliconiobic acid and silicotantallic acid. Among them, silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, tungstomolybdophosphoric acid, tungstomolybdosilicic acid,

15 acid, tungstovanadophosphoric acid, tungstovanadosilicic acid, molybdovanadosilicic acid, borotungstic acid, boromolybdic acid and boromolybdotungstic acid are especially preferred. Preferably, the acid content in the final catalyst is up to 50% by weight.

20 The final catalyst composition may suitably be optimised to maximise vinyl acetate production rate whilst maximising selectivity.

The catalyst of the present invention may suitably be prepared by the method described in detail in GB-A-1559540. In the first stage of the preparation process, the support is impregnated with a solution containing the required palladium and the promoter metal, for example gold, in the form of soluble salts.

25 Example of such salts include the soluble halide derivatives. The impregnating solution is preferably an aqueous solution and the volume of solution used is such that it corresponds to between 50 and 100% of the pore volume of the support, preferably 95 to 99% of the pore volume for fixed bed catalysts or 50 to 99% of the pore volume for fluid bed catalysts.

30 After impregnation, the wet support is, optionally, treated with an aqueous solution of an alkali metal salt selected from alkali metal silicates, carbonates or hydroxides to develop a metal shell structure familiar to those skilled in the art. The amount of alkali metal salt used is such that after the solution has been in contact with the impregnated support for between 12 and 24 hours, the pH of the

35 solution is suitably in the range 6.5 to 9.5, preferably 7.5 to 8 when measured at

25°C. The preferred metal salts are sodium metal silicate, sodium carbonate and sodium hydroxide.

During the treatment described above, palladium and promoter, for example gold, hydroxides are believed to be precipitated or incorporated onto the support. Alternatively, the impregnated support can be dried at ambient or reduced pressure and from ambient temperature to 150°C, preferably 60 to 120°C, prior to metals reduction. To convert such materials into the metallic state, the impregnated support is treated with a reducing agent such as ethylene, hydrazine, formaldehyde or hydrogen. If hydrogen is used, it will usually be necessary to heat the catalyst to 100 to 300°C in order to effect complete reduction.

After the steps described above have been carried out, the reduced catalyst is washed with water and then dried. The dried carrier is then impregnated with the required amount of vinyl acetate catalyst co-promoter, for example aqueous alkali metal acetate, and acetic acid catalyst promoter, for example aqueous selenium-containing compound, and thereafter dried. The dried carrier is further treated with an appropriate amount of heteropoly acid dissolved in water, and the final product dried.

The method of catalyst preparation may be varied to optimise catalyst performance based on maximising vinyl acetate yield and selectivity.

Preparation of vinyl acetate using the catalyst of the present invention is typically carried out by contacting ethylene, water and an oxygen-containing gas such as oxygen or air with the catalyst at a temperature of from 100 to 400°C, preferably 140 to 210°C and a pressure of 1 bar to 20 barg, preferably 6 to 15 barg.

The process may be carried out in a fixed bed or a fluidised bed reactor and is preferably carried out in the gas phase.

The present invention will now be illustrated with reference to the following Examples.

Example 1 is an example according to the present invention. Comparative Examples A, B and C are not according to the invention wherein the process utilised a catalyst not according to the present invention, Example A because it does not contain a vinyl acetate catalyst promoter or co-promoter, Example B because it does not contain an acid or an acetic acid catalyst promoter, and Example C because the acetic acid catalyst component and the vinyl acetate catalyst component are in separate beds.

Example 1**(a) Preparation of the Catalyst.**

In an aqueous solution containing 1.7g of sodium tetrachloropalladate (II) and 1.5g of sodium tetrachloroaurate (III) hydrate dissolved in 34g of water was placed 68.4g of a porous silica carrier (KA 160 ex Sud Chemie) having a particle size 5mm to 7mm to absorb the entire solution. The resultant carrier was added to 76.5g of an aqueous solution containing 6.5g of sodium metasilicate and covered completely by the solution. The mixture was allowed to stand for 18 hours and then 20g of 99% hydrazine hydrate was added to the solution to reduce Pd and Au.

The resultant mixture was allowed to stand for 4 hours or until the reduction was complete. The carrier was separated from solution and washed with deionised water until no chloride ion was found in the effluent using a AgNO_3 solution. The resultant carrier was dried at 60°C for 24 hours. In an aqueous solution containing 0.0071g of potassium selenate (VI) and 0.51g of potassium acetate dissolved in 5g of water was added 10g of the dried carrier. The carrier absorbed the entire solution and was dried at 60°C for 24 hours. Thereafter, an aqueous solution containing 3.3g of silicotungstic acid hydrate dissolved in 5g water was added to the carrier and absorbed entirely. The resultant carrier containing Pd, Au, selenium salt and silicotungstic acid was dried at 60°C for 24 hours.

20 Production of Vinyl Acetate

5g of the resultant catalyst was distributed evenly in 60mls glass beads (size 1mm) in a reaction tube. A mixture of ethylene, oxygen, steam and inert gas in a volume ratio of 40:6:31:23 was introduced into the unit at a temperature of 160°C and a pressure of 8 barg at a flow rate of 15.8 NL/hr to effect reaction. The effluent was analysed on line by gas chromatography. Vinyl acetate space time yield of 84.5 g/hr.L and selectivity of 76% was obtained based on carbon balance. CO_2 selectivity was 22%.

Comparative Example A**Preparation of Catalyst**

30 Sodium tetrachloropalladate (II)(9.5g) was dissolved in water (90g). A porous silica carrier (KA160 ex Sudchemie, particle size 5mm to 7mm) (180g) was impregnated with this aqueous solution until the entire solution was absorbed. The resultant carrier was added to an aqueous solution (170g) containing sodium metasilicate (17.7g). The mixture as allowed to stand for 18 hours and then 20g of 35 99% hydrazine hydrate was added to the solution to reduce the palladium. The

resultant mixture was allowed to stand for 4 hours or until the reduction was complete. The carrier was separated from the solution and washed with de-ionised water until no chloride ion was found in the effluent using a AgNO₃ solution. The resultant carrier was dried at 60°C for 48 hours. Potassium selenate (VI)(0.164g) was dissolved in water (10g) and was absorbed entirely by 20g of the dried carrier. Then the carrier was dried again at 60°C for 24 hours. Thereafter, an aqueous solution containing silicotungstic acid hydrate (6.3)g dissolved in water (10g) was added to the carrier and absorbed entirely. The resultant carrier containing palladium, selenium salt and silicotungstic acid was dried at 60°C for 24 hours.

Five gram of the resultant catalyst was distributed evenly in 60mls of glass beads (size 1mm) in a reaction tube, a mixture of ethylene, oxygen, steam and an inert gas in a volume ratio of 40:6:31:23 was introduced into the unit at a temperature of 150°C and a pressure of 8 bar G at a flow rate of 15.5Nl/hr to effect reaction. The effluent was analysed on line by gas chromatography.

As a result the following data was obtained: acetic acid space time yield of 235 g/hr.l, vinyl acetate space time yield of 2.1 g/hr.l, acetaldehyde space time yield of 3.5 g/hr.l and carbon dioxide space time yield of 21.2 g/hr.l. Overall selectivity to acetic acid was 87% and overall selectivity to vinyl acetate was 0.54%.

20 Comparative Example B

(a) Preparation of catalyst

Vinyl acetate catalyst prepared according to US 5185308 with nominal loadings of 0.9 Pd, 0.4 Au and 7 wt% KOAc on KA160.

Two and half gram of the resultant catalyst was distributed evenly in 60 mls of glass beads (size 1 mm) in a reaction tube, a mixture of ethylene, oxygen, steam and an inert gas in a volume ratio of 47:7:19:27 was introduced into the unit at a temperature of 150°C and a pressure of 8 bar G at a flow rate of 21.1Nl/hr to effect reaction. The effluent was analysed on line by gas chromatography.

As a result the following data was obtained carbon dioxide space time yield of 119.6 g/hr.l, no acetic acid, vinyl acetate or other by-products were detected.

30 Comparative Example C

(a) Preparation of catalyst

Catalysts were prepared according to Comparative Examples A and B.

(b) Production of Vinyl Acetate

35 A reaction tube was packed with Catalyst 1 (5g) and 2 (2.5g) and glass

beads (60ml, size 1mm). Catalyst 1 distributed evenly in glass beads (32ml) was placed in the upper part of the tube and Catalyst 2 in glass beads (16ml) at the lower. There were 2ml glass beads between Catalyst 1 section and Catalyst 2, and 5ml each at the top and the bottom of the tube. A mixture of ethylene, oxygen, steam and an inert gas in a volume ratio of 50:8:21:21 was introduced into the unit at a temperature of 150°C and a pressure of 8 bar G at a flow rate of 15.8Nl/hr to effect reaction. The effluent was analysed by on line gas chromatography.

The following results were obtained: vinyl acetate space time yield of 115 g/hr.l with a selectivity of 77% based on carbon balance, CO₂ selectivity of 11% and acetic acid selectivity of 5%. Ethyl acetate and ethanol were minor by-products.

It can be seen that reaction selectivities are only achieved which are comparable to those achieved from the claimed process when a two-stage process is operated.

Claims:

1. A catalyst for use in the production of vinyl acetate which comprises (1) a catalyst support, (2) palladium, (3) an acid, (4) at least one acetic acid catalyst promoter, and (5) at least one vinyl acetate promoter selected from the group consisting of cadmium acetate, gold, copper and nickel.
5
2. A catalyst as claimed in claim 1 in which the support comprises porous silica, alumina, silica/alumina, titania, zirconia or carbon.
10
3. A catalyst as claimed in either claim 1 or claim 2 in which the acid is a strong acid selected from a heteropolyacid.
4. A catalyst as claimed in claim 3 in which the acid content is up to 50% by weight.
15
5. A catalyst as claimed in any one of the preceding claims in which the acetic acid catalyst promoter is selected from selenium, titanium, tellurium and/or vanadium-containing compounds.
20
6. A catalyst as claimed in claim 5 in which the acetic acid catalyst promoter is an oxide, acetate or acetylacetonate.
7. A catalyst as claimed in any one of the preceding claims in which the vinyl acetate catalyst promoter is gold.
25

8. A catalyst as claimed in any one of the preceding claims further comprising at least one vinyl acetate co-promoter.
9. A catalyst as claimed in claim 8 in which the vinyl acetate catalyst co-
5 promoter is selected from alkali or alkali earth metal salts.
10. A catalyst as claimed in claim 9 in which the vinyl acetate co-promoter is sodium acetate or potassium acetate.
- 10 11. A process for the production of vinyl acetate which comprises reacting ethylene with an oxygen-containing gas and optionally water in the presence of a catalyst as claimed in any one of claims 1 to 10.
12. A process as claimed in claim 11 carried out at a temperature of from
15 100 to 400°C and under a pressure of 1 to 20 barg.