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Case 8588 (2)

SPECIFICATION

10

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PROCESS FOR THE PREPARATION OF
FLUID BED VINYL ACETATE CATALYST

20

BACKGROUND OF THE INVENTION

Field of the Invention

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This application is a continuation-in-part of U.S.
Serial No. 200,130 filed February 22, 1994.

30

The present invention relates to a process for
producing a fluid bed palladium-promoted catalyst useful in
the production of vinyl acetate from ethylene, acetic acid
and oxygen-containing gas. In addition, the present
invention relates to a novel fluid bed support and process
of using the support for the manufacture of palladium-
promoted fluid bed catalyst used in the manufacture of vinyl
acetate.

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The production of vinyl acetate by reacting ethylene,
acetic acid and oxygen together in the gas phase in the
presence of a catalyst is known. Typically, the catalysts

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are in fixed bed form and supported on a porous carrier material such as silica or alumina.

Early examples of these catalysts show that palladium and gold are distributed more or less uniformly throughout the carrier (see, for example, U.S. Patent Nos. 3,275,680, 3,743,607 and 3,950,400 and Great Britain Patent No. 1,333,449 and South African Patent No. 687,990).

Subsequently, it was recognized that this was a disadvantage since it was found that the material on the inner part of the carrier did not contribute to the reaction since the reactants did not significantly diffuse into the carrier.

To overcome this problem, new methods of catalyst manufacture were devised with the aim of producing catalyst in which the active components were concentrated on the outer-most shell of the support. For example, Great Britain Patent No. 1,500,167 claims catalyst in which at least ninety percent of the palladium and gold is distributed in that part of the carrier particle which is not more than thirty percent of the particle radius from the surface. In addition, Great Britain Patent No. 1,283,737 teaches that the degree of penetration into the porous carrier can be controlled by pre-treating the porous carrier with an alkaline solution of, for example, sodium carbonate or sodium hydroxide. Another approach which has been found to produce particularly active catalyst is described in U.S. Patent No. 4,048,096 and other methods of producing shell-impregnated catalyst are disclosed in U.S. Patent



Nos. 4,087,622 and 5,185,308. Each of these patents is primarily concerned with the manufacture of fixed bed catalyst useful for the manufacture of vinyl acetate.

However, U.S. Patent No. 3,950,400 also discloses that the catalyst disclosed therein may be used in a fluid bed reactor. In addition, Great Britain Patent No. 1,266,623 allegedly discloses a fluid bed catalyst for vinyl acetate manufacture which comprises palladium promoted with various alkali, alkaline earth or other metals.

It would be economically beneficial if the manufacture of vinyl acetate could be performed in a fluid bed process as well as a fixed bed process. Some of the typical benefits from a fluid bed process would be that the fluid bed reactor design is simpler than a multi-tubular fixed bed reactor, increased catalyst life is to be expected because no deactivation would take place due to hot spots which are typical of a fixed bed reactor, continuous addition of make-up catalyst can maintain peak performance and virtually eliminate catalyst change-outs, and higher production rates can be expected because substantially higher oxygen levels may be safely fed into the reactor without producing a flammable mixture.

Until the discovery of the process of the present invention, the preparation of palladium-promoted catalyst in fluid bed form has not led to catalyst having the necessary properties leading to a viable economical fluid bed process for the manufacture of vinyl acetate. The process of the

present invention overcomes the problems associated with the prior art resulting in a catalyst giving high performance and adequate attrition resistance so that it may be used in the manufacture of vinyl acetate.

5

Summary of the Invention

It is the primary object of the present invention to
10 provide a process for the manufacture of a fluid bed
palladium-metal-promoted alkali metal catalyst useful in the
manufacture of vinyl acetate.

It is another object of the present invention to
provide a novel support for use in the production of a fluid
15 bed palladium-metal-alkali-metal-promoted catalyst useful in
the fluid bed manufacture of vinyl acetate.

It is still another object of the present invention to
provide a novel process for the production of a support
useful in the manufacture of vinyl acetate catalyst.

20 Additional objects and advantages of the invention will
be set forth in part in the description which follows and,
in part, will be obvious from the description or may be
learned by practice of the invention. The objects and
advantages of the invention may be realized and attained by
25 means of the instrumentalities and combinations particularly
pointed out in the appended claims.

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To achieve the foregoing objects of the present invention, the process of manufacturing a fluid bed vinyl acetate catalyst characterized by the following formula comprising Pd-M-A wherein M equals barium, gold, 5 lanthanum, niobium, cerium, zinc, lead, calcium, strontium, antimony, or mixtures thereof; and A equals at least one alkali metal or mixture thereof comprises impregnating a pre-formed microspheroidal support wherein at least 50% of the particles have a particle size selected to be below 100 10 microns with a solution comprising a halide-free metal salt of the palladium, M and at least one alkali metal and drying the impregnated catalyst. The substantially inert particulate support typically comprises microspheroidal particles selected from the group consisting of alumina, 15 silica, zirconia, or mixtures thereof.

In another embodiment of the present invention the process is performed using an aqueous solution free or substantially free of any organic solvent.

In a preferred embodiment of the present invention the 20 metal salt of the alkali metal is separately impregnated onto the support, preferably subsequent to the impregnation of the solution comprising the salts of palladium and M element onto the support material.

In another embodiment of the present invention, the 25 impregnated support is heated under reducing conditions to form a deposit of palladium and M on the surface of the

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support. The reduction can take place either before or after the deposition of the alkali metal solution.

In a still further preferred embodiment of the present invention the catalyst is dried at a temperature below 80°C,
5 preferably between about 60° to 70°C.

In another preferred embodiment of the present invention the particle size (particle diameter) of the substantially inert support material is selected such that at least 50% of the particles are below about 60 microns.
10 Preferably, at least 75% of the particles are below 100 microns, especially preferred being at least 85% below 100 microns. Finally the preferred support is substantially free of sodium.

In another embodiment of the present invention, the
15 support for the manufacture of the vinyl acetate catalyst comprises a mixture of substantially inert microspheroidal particles having a pore volume of between 0.2 to 0.7cc/g, a surface area of between 100 to 200 m²/g and at least 50% of said particle are less than 100 microns.

20 In a preferred aspect of this embodiment of the present invention, at least 75% of the particles are below 100 microns, especially preferred being at least 85% below 100 microns.

In another embodiment of the present invention, the
25 support for the manufacture of the vinyl acetate catalyst comprises microspheroidal inert particles, preferably silica, zirconia, alumina or mixtures thereof wherein said



particles have a pore volume of between 0.2 to 0.7 cc/g, a surface area of between 100 to 200 m²/g and are obtained from a mixture of 80 to 20% inert support sol and 20 to 80% dried inert particles.

5 In a preferred embodiment of this aspect of the present invention, the pore volume of the inert particles is between 0.3 to 0.65 cc/g, especially preferred being 0.4 cc to 0.55 cc/gn.

10 In a further preferred embodiment of this aspect of the present invention, the surface area is between 110 to 195 m²/g, especially preferred being 120 to 195 m²/g.

In a further aspect of this embodiment of the present invention, the silica microspheroidal support material is manufactured by mixing between 20% to 80% silica sol with
15 80% to 20% silica aerosil, spray drying said mixture at an elevated temperature of between 125°C to 280°C, preferably 130° to 240°C, and calcining said spray dried particles preferably at a temperature of between 550° to 700°C, preferably between 630° to 660°C to form the support
20 material.

The substantially inert support for a fluid bed vinyl acetate catalyst may be manufactured by a process comprising mixing 80 to 20 wt% of an aqueous sol comprising substantially inert microspheroidal particles with 20 to
25 80 wt% of solid substantially inert particulate material to form an aqueous mixture, spray drying said aqueous mixture,

and calcining said particles to form said substantially inert support.

Typically, the weight percent of the palladium, M and alkaline in the catalyst of the present invention are: 0.1 to 5.0 wt% palladium, preferably 0.2 to 4.0 wt%, most preferably 0.3 to about 1.0 wt%; greater than 0 to 10 wt% alkali metal, preferably 0.1 to 8.0 wt%, most preferably 0.1 to 5.0 wt%; greater than 0 to about 5.0 wt% M, preferably 0.1 to about 4.0 wt%, most preferably 0.1 to 3.0 wt%.

10

Detailed Description of the Invention

Reference will now be made in detail to the present preferred embodiment of the invention of which the following examples are set forth for illustrative purposes only.

Reactor Testing

The catalysts were tested in a bench scale fluid bed reactor with a maximum catalyst capacity of 40 cc. Thirty cc of catalyst or catalyst-plus-diluent was the typical volume of solid loaded into the reactor. In general, sufficient catalyst was used such that the reactor contained 0.093 g of palladium metal with each catalyst evaluation. A total of 30 cc volume was obtained by mixing sufficient inert microspheroidal silica with the active catalyst prior to reactor testing. The reactor was equipped



with two feed inlets. For some of the experiments of this study, ethylene, acetic acid, and oxygen all entered the reactor through the lower inlet and nitrogen only was fed through the central inlet. In other tests, additional

5 oxygen was fed through the central feed inlet. This central inlet was located 2.5" above the lower feed inlet.

The reactor pressure was controlled at 115 psig and all lines leading to and from the reactor were heat traced and maintained at 150-155°C order to prevent condensation of
10 liquid feeds or products. Typical temperatures for the fluid bed reactor can vary from 100° to 250°C, preferably 135° to 190°C.

The gaseous reactor effluent was analyzed on-line using a Hewlett Packard Model 5890 gas chromatograph equipped with
15 both TCD and FID detectors. Oxygen, nitrogen, ethylene and carbon dioxide were separated on a 13x mole sieve column parallel with 10% carbowax 20M on 80/100 Chromosorb WAW and 23% SP2700 on 80/100 Chromosorb PAW, and quantitated with the TCD. Vinyl acetate and acetic acid were separated on a
20 4% carbowax 20M on 80/120 carbopack column and quantitated with the FID.



Support Preparation

Two types of preformed microspheroidal silica were prepared and utilized as supports in the practice of the present invention. Prior to use, all supports were sieved
5 and a specific particle size distribution of the support was used in all catalyst preparations:

5% of the particles are less than 105 microns
but greater than 88 microns

70% of the particles are less than 88 microns but
10 greater than 44 microns

25% of the particles are less than 44 microns

It should be understood the particle size distribution recited above is not intended to be limiting and that variations in this distribution are contemplated depending
15 upon reactor size and operating conditions.

Support 1

Support 1 was prepared by spray drying a mixture of Nalco (Nalco Chemical Company) silica sol 1060 and DeGussa
20 Aerosil® (DeGussa Chemical Company) silica. In the dried support, 80% of the silica came from the sol and 20% of the silica came from the Aerosil. The spray dried microspheres were calcined in air at 640°C for 4 hours.

Aerosil® silica is the trade name of Degussa's fumed
25 silica. This material has high surface area ($\sim 200 \text{ m}^2/\text{g}$), essentially no micropores, uniform particle size distribution in the nm-range (1×10^{-9} meter), and is free of

sodium. Fumed silica having properties comparable to Aerosil® may be produced by other companies and may be used in the place of Aerosil® in the preparation of Support 1.

5 Nalco silica sol 1060 is particularly advantageous for use in our application because of large mean particle size of the silica particles in the sol, 60 millimicrons. These larger silica particles pack less efficiently than smaller sol particles (~30 millimicrons as in Nalco 2327) and yield a final support higher in pore volume in the mesopore region
10 and lower in micropore volume. Other silica sols which have a similarly large (~40-80millimicron) mean particle size of the silica may be utilized in the place of the 1060 silica sol in the preparation of Support 1.

15 Support 2

A series of microspheroidal supports (Supports 2A-2D) containing KA-160 (Sud Chemie) were prepared as follows:

Support 2A: 75% SiO₂ from KA-160 with 25% SiO₂ from Sol

20 750 g of KA-160 was ground to pass through a 35 mesh screen and washed to remove any soluble impurities, such as chloride ions. This solid silica was then mixed with 694.4 g of Snotex-N-30 (Nissan Chemical) (36 wt% solids) silica sol and 556 g distilled water. This mixture was
25 milled overnight in a jar mill. The smooth slurry was then spray dried to form microspheroidal particles suitable for

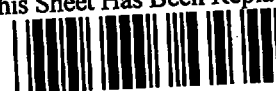


use in a fluid bed reactor. The microspheroidal support was then calcined at 640°C in air for 4 hours.

The role of the KA-160 support is to provide much of the pore structure within the microspheroidal particle. The
5 fixed bed support, KA-160, is produced by Sud Chemie and has properties which are advantageous for use in vinyl acetate catalyst preparation. Moderate surface area (160 m²/g), little or no microporosity, and substantial porosity (~0.57 cc/g) in the mesopore region are advantageous
10 properties of KA-160. Alternative fixed bed catalyst supports are available with surface area and pore volume properties similar to KA-160 (little or no micropores, mesopore volume of ~1.5-0.25 cc/g, and surface area 80-200 m²/g). These supports may be utilized in the place of
15 KA-160 in the preparation of Support 2.

Support 2B: 65% SiO₂ from KA-160 with 35% SiO₂ from Sol

This support was prepared in the same manner as Support 2A except that 227.5 g of KA-160, 408.3 g of
20 Snotex-N-30 (30 wt% solids) and 64 g of distilled water were used.



Support 2C: 50% SiO₂ from KA-160 with 50% SiO₂ from Sol

This support was prepared in the same manner as Support 2A except that 175 g of KA-160 and 583.3 g of Snotex-N-30 (30 wt% solids) were used.

5

Support 2D: 75% SiO₂ from KA-160 with 25% SiO₂ from Sol

This support was prepared in the same manner as Support 2A except that 262 g of KA-160, 219 g of Nalco 2327 (40 wt% solids) (Nalco Chemicals Company) and 219 g of distilled water were used.

10

Each type of microspheroidal silicas prepared above may be used advantageously in the preparation of fluid bed vinyl acetate monomer catalyst according to the process of the present invention. For use in the manufacture of fluid bed catalysts via impregnation with active metals, these supports provided unexpected superior physical properties for the vinyl acetate catalysts of the present invention compared to any readily available supports. Selected analytical data on all supports are included in Table 1 below.

15

20



TABLE 1
PHYSICAL PROPERTIES OF CUSTOMIZED
MICROSPHEROIDAL SILICA SUPPORTS

Support	Wt% Solids in Slurry	Pore Vol r≤4,500Å (cc/g)	Tot Pore Vol (cc/g)	Ap Bulk Density (g/cc)	SA m ² /g	Calcin Time/ Temp	Attrition Resist Loss 0-20 hrs
Support 1	.62	0.39	0.46	0.78	124.4	4 hr/ 640°C	<5%
Support 2A	50	0.60	0.60	0.65	175.5	4 hr/ 640°C	0.33%
Support 2B	50	0.39	0.39	0.72	184.4	4 hr/ 640°C	0.35%
Support 2C	46	0.27	0.33	0.77	191.9	4 hr/ 640°C	1.65%
Support 2D	50	0.62	0.63	0.60	156.0	4 hr/ 640°C	

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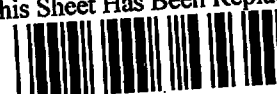
Catalyst Preparation

The general method utilized in the preparation is summarized below.

10

Typically, the microspheroidal support is impregnated with a solution (or solutions) of the active metals using the incipient wetness technique. Halide free compounds of the active metals, palladium, M element (e.g. gold) and potassium acetate, may be dissolved in the appropriate ratios in a suitable solvent, then impregnated upon the microspheroidal support. In general, it is desirable if all of the active metals to be used in a catalyst preparation are dissolved in a single portion of solvent which is of the volume just adequate to fill the pore volume of the support. In some instances a desired promoter may not be soluble in

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the same solvent as the other metal compounds to be used.

In this case a solution containing some of the metal components may be impregnated upon the support, followed by impregnating a second solution containing the remaining

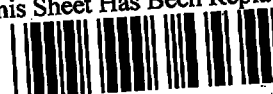
5 components. Solvents which are useful include water and volatile organic solvents such as: carboxylic acids with four carbons or less, alcohols, ethers, esters, and aromatics. After the wet catalyst is dried, it may be used for the production of vinyl acetate or it may first be
10 reduced by means known to those skilled in the art.

In general, when acetic acid is present and the catalyst is heated at an elevated temperature ($\sim 100^{\circ}\text{C}$) the catalyst darkens to black and becomes inactive.

Additionally, when a solution of palladium acetate (with or
15 without other metal acetates) is heated to too high a temperature or for too long, the solution changes color from the original red-orange to a greenish color and a black precipitate forms. In general, 60°C is a safe temperature to work at, but up to $\sim 80^{\circ}\text{C}$ has been used for brief periods
20 of time, to dissolve the palladium acetate.

Example 1

A catalyst having the following composition
0.75 wt% Pd, 0.32 wt% Au and 2.88 wt% K was prepared by
25 dissolving palladium acetate in an acetic acid solution of the gold acetate reagent described in U.S. Patent 4,933,204 and impregnating this combined solution upon a preformed



microspheroidal Support 2A identified above. The solid was dried at 60°C using a rotary evaporator (rotovap), then the Pd and Au were reduced with an aqueous solution of hydrazine (no alkali hydroxide). The solid was washed to
5 remove hydrazine, dried and potassium acetate was impregnated upon the solid. A 12.67g(16.7cc) charge of catalyst was placed in the reactor for testing. The results of reactor testing of this catalyst at various conditions are set forth below in Table 2. These results show an
10 18.2% conversion with 83% selectivity using 10.55 O₂, 14.31% HOAc, at 164.9°C.

Example 2

The catalyst of this example had a composition of
15 1.07 wt% Pd, 0.40 wt% Au and 2.89 wt% K and was prepared according to the procedure set forth in Great Britain Patent 1,266,623 except that the support was the same as used in Example 1. A 8.68g(11.3cc) charge of catalyst was placed in the reactor for testing. The results of testing
20 of this catalyst at various conditions is set forth below in Table 2 and gave 8.1% ethylene conversion and 84.4% vinyl acetate selectivity using 7% O₂, 10% HOAc, at 159°C.

Example 3

25 The procedure of Example 2 was repeated to produce a catalyst having a composition as follows: 1.01 wt% Pd, 0.38 wt% Au and 2.60 wt% K. However, Support 1 identified



above was utilized. A 9.2g(10.6cc) charge of catalyst was placed in the reactor for testing. The reactor testing at various conditions is set forth below in Table 2. The catalyst gave C_2H_4 conversion of 8.6 and VA selectivity of 85.3 under the same conditions as set forth in Example 2.

The performance of the catalyst of Examples 2 and 3 is very similar but the catalyst prepared on the Support 1 appears to be slightly more active. As the compositions of these two catalysts are nearly identical, the difference in activity may be due to the different supports.

Example 4

This catalyst was prepared according to the teachings of U.S. Patent 3,950,400 except that microspheroidal (fluid bed) Support 1 as described above was utilized. The composition was 0.82 wt% Pd, 0.40 wt% Au, 0.13 wt% Ba, 2.69 wt% K. The acetic acid was carefully removed under vacuum (using a rotovap) at 60°C. This solid remained tan in color. A 11.57g(13.4cc) charge of catalyst was placed in the reactor for testing. Reactor testing of this catalyst set forth in Table 2 demonstrated it to be highly active and selective. At 164°C using 7% oxygen and 14% acetic acid, 12.5% ethylene conversion was obtained with 87.2% selectivity.

Example 5



A catalyst having the following composition: Pd 0.81 wt%, 0.34 wt% Au and 2.71 wt% K was prepared by dissolving palladium acetate (PdAc) and potassium acetate (KAc) in acetic acid, then adding gold acetate and impregnating it on
5 Support 1. The acetic acid was removed under vacuum, at 60°C. This solid was tan in color at this point. The preparation of this catalyst is similar to that of Example 1 except there was no catalyst reduction prior to testing. A 11.75g(13.2cc) charge of catalyst was placed in the reactor
10 for testing. The results of testing this catalyst under various conditions is set forth in Table 2. The catalyst gave 9.2% conversion with 87.8% VA selectivity.

Example 6

15 A catalyst having the following composition: 0.77 wt% Pd, 0.40 wt% Au and 2.2 wt% K was prepared as with Example 5. The solid was then subjected to a hydrazine reduction, washed with water to remove hydrazine, and additional potassium acetate was added. A 14.25g(17.6cc)
20 charge of catalyst was placed in the reactor for testing. Excellent reactor results were obtained as shown in Table 2. This catalyst gave similar results, 10.17% conversion with 85.7% selectivity, as compared with Example 5.

A variety of Pd/M/K on silica-type catalysts were
25 prepared wherein M is not gold. Metals evaluated included M =Ba, La, Sb, Pb, Ce, Nb, Ca, Zn, and Sr. The following examples are illustrative of these various metals.



Example 7

The catalyst was prepared with the lower level of palladium which is typically used with Bayer-type catalysts, 0.88 wt% Pd, but which is typically too inactive for use with Hoechst-type catalysts along with 0.88 wt% Ba. Acetic acid was the solvent. The catalyst had 2.9 wt% K. A 15.52g(21.0cc) charge of catalyst was placed in the reactor for testing. The results of testing conversions approaching 10% ethylene with 81% selectivity to VA were obtained under various conditions as set forth below in Table 2. The catalyst suffered some deactivation by exposure to an elevated temperature (100°C) while acetic acid was still present.

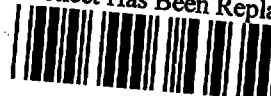
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Example 8

A catalyst having 0.41 wt% Pd, 0.49 wt% Ba and 2.2 wt% K was prepared using water as the sole solvent. The mixture of palladium acetate, potassium acetate and barium acetate is sufficiently soluble in distilled water that water can be used as the sole solvent. A 24.77g(30.0cc) charge of catalyst was placed in the reactor for testing. Reactor testing of this catalyst under various conditions is set forth below in Table 2 and gave 10% ethylene conversion at 85% selectivity to VAM.

25

The use of water as the impregnating solvent instead of acetic acid has several significant advantages. Water is



certainly less expensive, less toxic and less corrosive than acetic acid. All of which will give a less expensive process using water. Additionally, water does not act as a reducing agent for the palladium. When heated at 100°C in the oven, the catalyst prepared with acetic acid darkened to near black, whereas the analogous catalyst prepared in water, retained its tan color and still retained its excellent reactor performance. Finally, water would be a more benign solvent with respect to any detrimental effects upon the support.

Example 9

A solution of palladium acetate, potassium acetate and antimony acetate in acetic acid were impregnated upon the preformed microspheroidal support. The wet solid was dried at 60°C under vacuum. No pre-reduction of the catalyst was performed. The resulting catalyst comprised 0.81 wt% Pd, 0.70 wt% Sb and 2.9 wt% K. A 10.95g(12.8cc) charge of catalyst was placed in the reactor for testing. Reactor testing shown in Table 2 gave ethylene conversions of nearly 17% with 89% selectivity at only 9 mole% oxygen in the feed mixture.

Example 10

The addition of barium to an antimony containing catalyst substantially reduced catalyst activity. The catalyst tested had a composition (wt%) of 0.71 Pd, 0.71 Ba,



0.71 Sb and 2.6 K. A 10.95g(13.5cc) charge of catalyst was placed in the reactor for testing. There is no synergy between the antimony and the barium at the levels evaluated as shown by the results in Table 2 below.

5

Examples 11 and 12

A mixture of palladium acetate, lanthanum acetate and potassium acetate was quite soluble in acetic acid.

Support 1 was used for Example 11 and Support 2A for

10 Example 12. This solution impregnated upon the preformed support and dried under vacuum resulted in an excellent catalyst as shown in Table 2 below. The composition of catalysts 11 and 12, respectively, in weight percent were as follows: 0.77 Pd, 0.70 La, 2.7 K; 0.80 Pd, 0.57 La, 3.1 K.

15 For example 11 a 10.95g(13.0cc) charge of catalyst was placed in the reactor for testing. For example 12 a 10.95g(15.0cc) charge of catalyst was placed in the reactor for testing. Conversions and selectivities were slightly lower than with the antimony-containing catalyst, but were
20 still very good.

Example 13

The mixture of palladium acetate, lanthanum acetate and potassium acetate was dissolved in water instead of acetic
25 acid resulting in a catalyst having the following composition: 0.15 wt% Pd, 0.34 wt% La, 1.4 wt% K. A 25.2g (30.0cc) charge of catalyst was placed in the reactor for



testing. Considering the low level of palladium present, the ethylene conversion of 8% as shown in Table 2 was quite good.

5 Example 14

Niobium oxalate, the source of niobium utilized, was insoluble in acetic acid. For that reason the niobium oxalate was pre-impregnated onto Support 1 using an aqueous solution. After drying the support, an acetic acid solution
10 of palladium acetate and potassium acetate was impregnated upon the support. A 11.04g(14.0cc) charge of catalyst was placed in the reactor for testing. Resulting catalyst composition was 0.81 wt% Pd, 0.64 wt% Nb, 3.1 wt% K. Reactor performance was adequate at ~9% conversion and
15 84% selectivity, but this catalyst appeared to deactivate more rapidly than expected.

Examples 15 and 16

Calcium was added as the promoter at two different
20 levels: (1) the same mole % as barium in Example 7, and (2) at near the wt% level as barium in Example 7. In each case, Support 2A was used. For example 15 a 10.95g(15.8cc) charge of catalyst was placed in the reactor for testing. For example 16, a 10.95g(15.4cc) charge of catalyst was
25 placed in the reactor for testing. Neither catalyst performed well as shown in Table 2, but the lower level of calcium gave higher conversions and higher selectivities.



It is possible that adjusting the calcium level further could improve catalyst performance.

Examples 17 and 18

5 Cerium promoted catalyst (Example 17) and zinc promoted catalyst (Example 18) were prepared as described in the general procedure set forth above with the metals being dissolved in acetic acid and drying at 60°C under vacuum. In each case, Support 2A was utilized. The final
10 composition of the catalyst were: Example 17--0.80 wt% Pd, 0.69 wt% Ce, 2.8 wt% K; Example 18--0.81 wt% Pd, 0.33 wt% Zn and 2.9 wt% K. A 10.96g(15.6cc) charge of catalyst was placed in the reactor for testing for example 17. For example 18, a 10.96g(15.6cc) charge was used. Tests of
15 these catalysts showed potential as shown in Table 2. Optimization of promoter level and reduction treatment could be beneficial. In particular, cerium showed very good initial activity.

20 Examples 19 and 20

The catalyst of Examples 19 and 20 were prepared on the same support and utilizing substantially the same procedure set forth in Examples 17 and 18 above except that Pb and Sr were substituted for Ce and Zn. The final
25 composition of Example 19 on a wt% basis was 0.81 Pd, 0.70 Pb, 2.9 K. The final composition of Example 20 on a wt% basis was 0.80 Pd, 0.68 Sr, 2.7 K. For example 19 a



11.71g(13.2cc) charge of catalyst was placed in the reactor for testing. In example 20 a 10.95g(15.4cc) charge was used. As shown in Table 2, the lead promoted catalyst appeared to deactivate more rapidly than expected, while the
5 strontium promoted catalyst was of low activity and poor selectivity.



TABLE 2

RUN DATA SUMMARY --- FLUID BED VAM IMPREGNATED CATALYSTS										
RUN #	% C ₂ H ₄	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O ₂	N ₂	C ₂ H ₄	HOAC		
Example 1										
1	14.42	85.38	163.0	396.41	7.040	30.65	47.930	14.380	115	0.8
2	14.87	87.16	161.5	396.41	7.040	30.65	47.930	14.380	115	2.4
3	14.46	86.00	161.9	396.41	7.040	30.65	47.930	14.380	115	2.9
4	18.20	83.06	164.9	396.41	10.550	27.17	47.970	14.310	115	3.9
5	17.95	86.86	161.7	418.63	10.010	31.17	45.390	13.430	115	6.0
6	17.38	88.86	155.5	418.63	10.010	31.17	45.390	13.430	115	6.3
7	17.57	87.80	158.2	418.63	10.010	31.17	45.390	13.430	115	6.9
8	17.01	88.05	157.2	418.63	10.010	31.17	45.390	13.430	115	7.2
9	19.03	85.21	165.2	426.13	11.590	30.62	44.590	13.200	115	7.6
Example 2										
1	7.54	82.59	159.4	361.70	7.460	29.31	52.810	10.420	115	1.5
2	7.67	82.99	160.4	361.70	7.460	29.31	52.810	10.420	115	1.8
3	7.79	83.77	159.8	361.70	7.460	29.31	52.810	10.420	115	2.0
4	7.96	84.20	160.0	361.70	7.460	29.31	52.810	10.420	115	2.3
5	7.97	84.28	159.6	361.70	7.460	29.31	52.810	10.420	115	2.6
6	8.05	84.43	159.6	361.70	7.460	29.31	52.810	10.420	115	3.0
7	4.32	88.03	154.4	365.00	7.370	29.97	52.330	10.330	115	4.4
8	4.82	85.51	160.4	365.00	7.370	29.97	52.330	10.330	115	5.4
9	4.88	85.55	160.9	365.00	7.370	29.97	52.330	10.330	115	5.8
10	4.93	85.61	160.9	365.00	7.370	29.97	52.330	10.330	115	6.1
11	6.19	86.15	159.1	365.00	7.370	29.97	52.330	10.330	115	8.3
12	6.17	86.03	159.1	365.00	7.370	29.97	52.330	10.330	115	8.7

RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
13	6.18	85.97	159.1	365.00	7.370	29.97	52.330	10.330	115	9.1
14	6.39	84.54	161.0	365.00	7.370	29.97	52.330	10.330	115	9.5
15	6.54	85.10	161.0	365.00	7.370	29.97	52.330	10.330	115	9.8
16	6.66	85.40	161.0	365.00	7.370	29.97	52.330	10.330	115	10.2
Example 3										
1	8.83	84.17	160.0	362.80	7.610	29.36	52.650	10.390	115	1.7
2	8.81	84.65	159.0	362.80	7.610	29.36	52.650	10.390	115	2.5
3	8.68	85.17	159.0	362.80	7.610	29.36	52.650	10.390	115	3.6
4	8.64	85.30	159.0	362.80	7.610	29.36	52.650	10.390	115	4.1
Example 4										
1	11.48	88.68	162.0	396.41	7.040	30.65	47.930	14.380	115	3.7
2	11.49	87.63	162.0	396.41	7.040	30.65	47.930	14.380	115	4.1
3	12.46	87.24	164.0	396.41	7.040	30.65	47.930	14.380	115	4.5
4	12.76	86.06	165.0	396.41	7.040	30.65	47.930	14.380	115	4.9
Example 5										
1	7.64	87.33	158.7	396.41	7.040	30.65	47.930	14.380	115	0.5
2	9.17	87.84	161.0	396.41	7.040	30.65	47.930	14.380	115	0.9
3	8.64	89.49	157.0	396.41	7.040	30.65	47.930	14.380	115	1.3
Example 6										
1	9.89	84.22	161.3	363.60	7.450	29.65	52.530	10.369	115	5.1
2	10.45	83.70	163.1	363.60	7.450	29.65	52.530	10.369	115	5.6
3	10.14	85.54	160.0	363.60	7.450	29.65	52.530	10.369	115	6.1
4	10.17	85.65	159.2	363.60	7.450	29.65	52.530	10.369	115	6.6
5	14.53	85.18	161.0	382.60	10.795	24.49	49.922	14.794	115	10.3

RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
6	14.84	85.46	160.0	382.60	10.795	24.49	49.922	14.794	115	10.8
7	15.30	85.84	159.6	382.60	10.795	24.49	49.922	14.794	115	11.2
8	17.23	87.88	159.6	382.60	10.795	24.49	49.922	14.794	115	11.7
9	15.52	85.98	159.6	382.60	10.795	24.49	49.922	14.794	115	12.2
Example 7										
1	9.38	78.05	162.7	363.90	7.610	29.60	51.940	10.850	115	0.8
2	9.74	80.27	160.8	363.90	7.610	29.60	51.940	10.850	115	1.6
3	9.77	80.97	160.6	363.90	7.610	29.60	51.940	10.850	115	2.6
4	9.62	81.73	160.6	363.90	7.610	29.60	51.940	10.850	115	3.6
5	9.67	82.93	159.8	363.90	7.610	29.60	51.940	10.850	115	4.5
Example 8										
1	10.61	85.55	161.0	362.30	7.730	29.70	52.170	10.410	115	2.0
2	9.83	85.42	161.0	362.30	7.730	29.70	52.170	10.410	115	4.0
Example 9										
1	14.75	88.30	158.0	408.20	7.450	31.97	46.790	13.790	115	2.2
2	14.70	88.90	157.0	408.20	7.450	31.97	46.790	13.790	115	2.6
3	14.69	89.60	157.0	408.20	7.450	31.97	46.790	13.790	115	2.9
4	14.44	89.90	157.0	408.20	7.450	31.97	46.790	13.790	115	3.3
5	16.63	88.30	158.0	414.90	8.940	31.45	46.040	13.570	115	3.8
6	17.15	88.50	158.0	414.90	8.940	31.45	46.040	13.570	115	4.1
7	16.93	89.20	158.0	414.90	8.940	31.45	46.040	13.570	115	4.5
8	16.09	89.30	157.0	414.90	8.940	31.45	46.040	13.570	115	4.8
9	16.94	88.20	160.0	414.90	8.940	31.45	46.040	13.570	115	5.2
10	17.14	88.40	160.0	414.90	8.940	31.45	46.040	13.570	115	5.6
11	16.87	89.10	160.0	414.90	8.940	31.45	46.040	13.570	115	5.9

RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psi g	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
12	16.54	89.20	160.0	414.90	8.940	31.45	46.040	13.570	115	6.3
13	14.54	88.70	163.0	418.60	9.680	31.18	45.630	13.520	115	9.8
14	14.39	88.80	162.0	418.60	9.680	31.18	45.630	13.520	115	10.1
15	14.10	89.10	161.0	418.60	9.680	31.18	45.630	13.520	115	10.5
16	15.10	88.10	165.0	418.60	9.680	31.18	45.630	13.520	115	10.8
17	15.13	87.60	165.0	418.60	9.680	31.18	45.630	13.520	115	11.2
18	15.71	87.60	168.0	418.60	9.680	31.18	45.630	13.520	115	11.5
19	15.19	87.60	166.0	418.60	9.680	31.18	45.630	13.520	115	11.9
Example 10										
1	1.90	91.40	154.0	418.30	9.980	31.20	45.660	13.460	115	3.0
2	1.99	90.90	154.0	418.30	9.980	31.20	45.660	13.460	115	3.3
3	2.73	88.50	162.0	418.30	9.980	31.20	45.660	13.460	115	3.6
4	3.52	87.30	163.0	418.30	9.980	31.20	45.660	13.460	115	4.0
5	4.61	86.80	163.0	418.30	9.980	31.20	45.660	13.460	115	4.3
6	6.53	82.00	169.0	418.30	9.980	31.20	45.660	13.460	115	4.7
7	7.75	80.70	173.0	418.30	9.980	31.20	45.660	13.460	115	5.0
8	8.73	80.60	176.0	418.30	9.980	31.20	45.660	13.460	115	5.4
9	8.93	82.10	175.0	418.30	9.980	31.20	45.660	13.460	115	5.7
Example 11										
1	13.27	86.90	159.0	408.20	7.450	31.97	46.790	13.790	115	1.3
2	13.89	87.00	159.0	408.20	7.450	31.97	46.790	13.790	115	1.6
3	13.88	87.20	159.0	408.20	7.450	31.97	46.790	13.790	115	2.0
4	13.88	87.30	159.0	408.20	7.450	31.97	46.790	13.790	115	2.3
5	13.74	87.40	159.0	408.20	7.450	31.97	46.790	13.790	115	2.6
6	15.82	85.30	162.0	418.30	9.980	31.20	45.660	13.460	115	3.5
7	15.96	84.80	162.0	418.30	9.980	31.20	45.660	13.460	115	3.9

RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
8	15.64	85.30	161.0	418.30	9.980	31.20	45.660	13.460	115	4.2
9	15.65	85.70	160.0	418.30	9.980	31.20	45.660	13.460	115	4.5
10	16.28	84.50	164.0	418.30	9.980	31.20	45.660	13.460	115	4.9
11	16.28	84.60	165.0	418.30	9.980	31.20	45.660	13.460	115	5.2
12	16.51	84.70	165.0	418.30	9.980	31.20	45.660	13.460	115	5.6
13	16.51	84.70	165.0	418.30	9.980	31.20	45.660	13.460	115	5.8
Example 12										
1	13.46	83.11	159.6	407.63	6.750	32.50	46.980	13.770	115	1.4
2	13.88	84.15	159.6	407.63	6.750	32.50	46.980	13.770	115	1.8
3	13.85	84.39	159.0	407.63	6.750	32.50	46.980	13.770	115	2.2
4	14.01	84.91	159.0	407.63	6.750	32.50	46.980	13.770	115	2.7
5	13.67	85.31	158.0	407.63	6.750	32.50	46.980	13.770	115	3.1
6	13.96	84.51	163.5	421.03	9.710	31.47	45.480	13.330	115	4.8
7	13.03	85.43	160.0	421.03	9.710	31.47	45.480	13.330	115	5.6
8	12.35	85.95	159.0	421.03	9.710	31.47	45.480	13.330	115	6.5
9	11.90	86.00	157.0	421.03	9.710	31.47	45.480	13.330	115	6.9
10	11.54	86.24	156.0	421.03	9.710	31.47	45.480	13.330	115	7.3
11	11.41	86.62	156.0	421.03	9.710	31.47	45.480	13.330	115	7.8
Example 13										
1	8.90	84.34	157.2	421.91	9.690	31.40	45.390	13.510	115	0.8
2	8.54	83.98	156.0	421.91	9.690	31.40	45.390	13.510	115	1.5
3	8.22	84.26	163.2	421.91	9.690	31.40	45.390	13.510	115	2.5
4	7.42	84.87	157.4	421.91	9.690	31.40	45.390	13.510	115	3.4
5	6.97	85.27	156.5	421.91	9.690	31.40	45.390	13.510	115	4.2



RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
Example 14										
1	10.74	81.77	164.4	408.07	6.739	32.47	46.928	13.863	115	0.5
2	9.98	84.55	161.1	408.07	6.739	32.47	46.928	13.863	115	0.9
3	9.24	86.01	159.0	408.07	6.739	32.47	46.928	13.863	115	1.4
4	10.61	83.39	165.0	421.47	9.704	31.44	45.436	13.422	115	4.0
5	10.13	83.92	165.8	421.47	9.704	31.44	45.436	13.422	115	4.4
6	8.69	86.00	162.0	421.47	9.704	31.44	45.436	13.422	115	5.3
Example 15										
1	7.45	83.44	159.0	408.07	6.739	32.47	46.928	13.863	115	0.9
2	7.47	84.09	158.0	408.07	6.739	32.47	46.928	13.863	115	1.3
3	7.15	84.60	158.0	408.07	6.739	32.47	46.928	13.863	115	1.8
4	6.63	85.15	157.0	408.07	6.739	32.47	46.928	13.863	115	2.6
5	7.60	82.18	159.0	421.47	9.704	31.44	45.436	13.422	115	3.9
6	6.99	82.28	159.0	421.47	9.704	31.44	45.436	13.422	115	4.8
7	6.14	83.52	158.0	421.47	9.704	31.44	45.436	13.422	115	6.0
Example 16										
1	4.78	80.03	155.6	408.51	6.730	32.43	46.880	13.960	115	2.5
Example 17										
1	11.99	85.37	159.5	408.51	6.730	32.43	46.880	13.960	115	1.5
2	11.68	85.86	159.5	408.51	6.730	32.43	46.880	13.960	115	1.9
3	11.41	86.28	158.0	408.51	6.730	32.43	46.880	13.960	115	2.3
4	10.95	87.07	156.3	408.51	6.730	32.43	46.880	13.960	115	2.7
5	10.29	87.36	156.6	408.51	6.730	32.43	46.880	13.960	115	3.2
6	11.38	86.38	157.3	421.91	9.694	31.41	45.389	13.512	115	3.6
7	11.60	85.38	159.0	421.91	9.694	31.41	45.389	13.512	115	4.5



RUN #	% C2H4	% VA	BED T	TOTAL	FEED COMPOSITON				Psig	HRS
	CONV	SEL	(C)	FLOW	O2	N2	C2H4	HOAC		
8	11.11	85.98	158.9	421.91	9.694	31.41	45.389	13.512	115	5.3
9	10.52	86.48	159.9	421.91	9.694	31.41	45.389	13.512	115	6.2
Example 18										
1	12.01	80.41	170.0	408.51	6.730	32.43	46.880	13.960	115	1.1
2	10.91	85.10	156.7	408.51	6.730	32.43	46.880	13.960	115	1.6
3	12.39	84.94	159.0	421.91	9.694	31.41	45.389	13.512	115	2.4
4	10.89	84.98	161.0	421.91	9.694	31.41	45.389	13.512	115	3.3
5	11.13	85.42	161.0	421.91	9.694	31.41	45.389	13.512	115	3.7
6	10.12	86.21	159.0	421.91	9.694	31.41	45.389	13.512	115	5.0
7	8.68	88.28	156.0	421.91	9.694	31.41	45.389	13.512	115	6.7
8	7.41	89.84	154.7	421.91	9.694	31.41	45.389	13.512	115	9.3
Example 19										
1	10.66	84.76	162.9	408.51	6.730	32.43	46.880	13.960	115	1.4
2	9.34	85.79	158.5	408.51	6.730	32.43	46.880	13.960	115	2.3
3	8.82	86.11	158.5	421.91	9.694	31.41	45.389	13.512	115	3.1
4	7.34	87.94	158.5	421.91	9.694	31.41	45.389	13.512	115	4.4
Example 20										
1	6.06	82.27	156.8	408.51	6.730	32.43	46.880	13.960	115	1.4
2	5.66	83.00	156.8	408.51	6.730	32.43	46.880	13.960	115	3.1
3	5.11	83.60	156.8	408.51	6.730	32.43	46.880	13.960	115	6.1



Claims:

1. A support for the manufacture of a vinyl acetate catalyst comprising a mixture of substantially inert microspheroidal particles having a pore volume of between 0.2 to 0.7 cc/g, a surface area of between 100 to 200 m²/g and at least 50% of said particles are less
5 than 100 microns.
2. A support as claimed in claim 1 wherein the pore volume is between 0.3 and 0.65 cc/g, the surface area is between 100 to 195 m²/g and at least 75% of the particles are below 100 microns.
3. A support as claimed in claim 1 or claim 2 wherein the
10 substantially inert microspheroidal particles are selected from the group consisting of silica, zirconia, alumina and mixtures thereof.
4. A support as claimed in claim 1 or claim 2 wherein the substantially inert microspheroidal particles are selected to be silica.
- 15 5. A process for the manufacture of a substantially inert support for a fluid bed vinyl acetate catalyst comprising mixing 80 to 20 wt% of an aqueous sol comprising substantially inert microspheroidal particles with 20 to 80 wt% solid substantially inert particulate material to form an aqueous mixture, spray drying said aqueous
20 mixture, and calcining said particles to form said substantially inert support.
6. A process as claimed in claim 5 wherein said substantially inert particles in the aqueous sol are selected from the group consisting of silica, alumina, and zirconia.
- 25 7. A process as claimed in claim 5 wherein said substantially





inert particles in the aqueous sol are selected to be silica.

8. A process for the manufacture of a fluid bed vinyl acetate catalyst characterised by the formula Pd-M-A wherein M equals Ba, Au, La, Nb, Ce, Zn, Pb, Ca, Sr, Sb or mixtures thereof and A equals at least one alkali metal comprising impregnating a preformed microspheroidal substantially inert support with an aqueous solution substantially free of organic solvent comprising halide-free metal salt of Pd, M and at least one alkali metal and drying the impregnated microspheroidal support.
9. A process for manufacturing a fluid bed vinyl acetate catalyst characterised by the following formula comprising Pd-M-A wherein M equals barium, gold, lanthanum, niobium, cerium, zinc, lead, calcium, strontium, antimony, or mixtures thereof; and A equals at least one alkali metal, comprising impregnating a pre-formed substantially inert microspheroidal particulate support wherein at least 50% of the particles have a size below 100 microns with a solution comprising a halide-free metal salt of the palladium, M, and at least one alkali metal and drying the impregnated pre-formed support.
10. A process as claimed in claim 9 wherein at least 75% of the microspheroidal support particles are below 100 microns.
11. A process as claimed in any one of claims 8 to 10 wherein the substantially inert microspheroidal particles are selected from the group consisting of silica, zirconia, alumina and mixtures thereof.
12. A process as claimed in any one of claims 8 to 11 wherein the alkali metal is separately impregnated onto the microspheroidal support material prior to drying the support.
13. A process as claimed in claim 12 wherein the alkali metal is impregnated onto the microspheroidal support subsequent to impregnating the support with the solution comprising the halide-free salts of palladium and M.
14. A process as claimed in any one of the claims 8 to 13 which further comprises drying the catalyst at a temperature up to about 80°C.
15. A process as claimed in any one of claims 8 to 14 wherein M is selected to be antimony.





16. A process as claimed in any one of claims 8 to 14 wherein M is selected to be gold in the absence of barium.
17. A process as claimed in any one of claims 9 to 16 wherein the solution comprising a halide-free metal salt of the palladium, M and at least one alkali metal is an aqueous solution substantially free of organic solvent.
18. A process as claimed in any one of claims 8 to 17 wherein the inert microspheroidal particulate support is a support as claimed in any one of claims 1 to 4 or is a support manufactured by a process as claimed in any one of claims 5 to 7.
19. A fluid bed vinyl acetate catalyst characterised by the following formula comprising Pd-M-A wherein M equals barium, gold, lanthanum, niobium, cerium, zinc, lead, calcium, strontium, antimony, or mixtures thereof; and A equals at least one alkali metal impregnated on a pre-formed substantially inert microspheroidal particulate support wherein at least 50% of the particles have a size below 100 microns.
20. A catalyst as claimed in claim 19 wherein at least 75% of the microspheroidal support particles are below 100 microns.
21. A catalyst as claimed in any one of claims 19 to 20 wherein the substantially inert microspheroidal particles are selected from the group consisting of silica, zirconia, alumina and mixtures thereof.
22. A catalyst as claimed in any one of claims 19 to 21 wherein M is selected to be antimony.
23. A catalyst as claimed in any one of claims 19 to 22 wherein the support is a support as claimed in any one of claims 1 to 4 or is a support manufactured by a process as claimed in any one of claims 5 to 7.
24. A process for the production of vinyl acetate which comprises reacting ethylene, acetic acid and oxygen together in the gas phase in the presence of a fluidized bed of catalyst wherein the catalyst is a catalyst manufactured by a process as claimed in any one of claims 8 to 18 or is a catalyst as claimed in any one of claims 19 to 23.

