

Synthesis reactor with a catalyst for the Synthesis of Vinyl Acetate in the Gas Phase

[0001] The invention relates to a synthesis reactor with a catalyst for the production of monomeric vinyl acetate (VAM), by which gaseous ethylene and gaseous acetic acid as well as oxygen or gases containing oxygen react catalytically, the catalyst being a catalyst for use as a wall catalyst in a synthesis reactor for producing vinyl acetate, the synthesis reactor being characterised in that a catalyst is adhesively applied to the wall surfaces of the reaction chambers by way of an oxidic or organic binding agent in a synthesis reactor that is made of stainless steel.

[0002] The prior art comprehensively describes the synthesis of vinyl acetate from ethylene. For this, ethylene, acetic acid and molecular oxygen or gases containing O₂, possibly with the addition of inert gases such as CO₂, for example, are brought to reaction in the presence of a catalyst at temperatures of 100 °C to 250 °C and increased pressure. This is done by passing the process gas over a catalyst bed. For this strongly exothermic reaction a catalyst containing palladium, gold and alkali metals on an oxidic carrier is normally used. The catalyst is in the form of moulded bodies, such as spheres, granulate, tablets or extrudates onto which the catalytically active substances are applied in a shell-shaped outer zone.

[0003] EP 1 106 247 B1 describes such a method and a suitable catalyst whereby the carrier catalyst has an ideal Pd proportion of 0.3 to 4.0% by weight and an Au content of 0.1 to 2.0% by weight. The thickness of the catalyst on the carrier is given as max. 1 mm, and is preferably less than 0.5 mm. EP 1 106 247 B1 cites productivities (designated as activity in the patent specification) of max. 225.5 g_{VAM}/kg_{cat}*h. Although high selectivity is mentioned in the patent specification, it is not described or quantified as a function of the selected carrier catalyst or the preparation method. In EP 0 987 058 B1 a silicon dioxide-based carrier catalyst is described which has a special carrier geometry.

[0004] Various synthesis catalysts which are known in the prior art are set forth in DE 190 20 390. In DE 198 34 569 A1 doping with hafnium is proposed which has resulted in high productivities of up to 1100 g_{VAM}/l_{cat}*h at 9 bars, 170°C and 0.5% by weight Hf loading.

[0005] DE 199 14 066 discloses a catalyst in which barium or cadmium are used as doping elements and various metal oxides are used in the carrier body. The use of cadmium is detrimental on environmental grounds.

[0006] From DE 196 19 961, EP 0 916 402 A1 or EP 0 997 192 B1 optimising the external shape of the carrier bodies is also known. Mouldings, cylinders, ring and other shapes used in VAM synthesis are known. In EP 1 323 469 A3 a moulded body is described which as a pyrogenically produced silicon dioxide body has special open structures. In EP 1 106 247 B1 external dimensions of 2-15 mm are given for such moulded bodies. The loading is given as 0.2-1.5% by weight Au, 0.3-4.0% by weight Pd and 3.5-10% by weight potassium acetate.

[0007] In EP 0 997 291 B1 carrier materials are cited which comprise at least two components from the SiO_2 , Al_2O_3 , TiO_2 and ZrO_2 group. According to the aforementioned patent specification these carrier materials can be of any shape, e.g. cylinders, spheres or rings which are produced as extruded parts, extrudates or tablets. Also in EP 0 723 810 B1 a carrier material is disclosed that contains the elements zirconium and titanium. As an advantage of the invention the examples show that a productivity of 225 $\text{g}_{\text{VAM}}/\text{kg}_{\text{cat}}\cdot\text{h}$ is achieved.

[0008] It is also known and described in the prior art that a number of by-products are formed during the synthesis of VAM. In DE 199 20 390 the substances CO_2 , ethyl acetate and high boilers such as ethylidene diacetate, ethylene glycol and its acetates or diacetoxymethylene are cited. In this patent specification a catalyst is described which beneficially influences selectivity with regard to the high boilers by adding vanadium.

[0009] It is also known that in the production of vinyl acetate considerable effort is required to separate the product from the educts and by-products following the synthesis stage. Separation normally takes place by means of post-synthesis distillation and other steps to separate the material streams. DE 39 34 614 A1 describes vinyl acetate synthesis with different processing stages for subsequent product treatment, wherein 1000-2000 ppm by weight is given as the known limit value for ethyl acetate and a target residual content of ethyl acetate of 150 ppm by weight is cited.

[0010] EP 0 072 484 discloses a method which through the addition of small quantities of H_2O into a vinyl acetate return flow and its introduction in the distillation plant leads to better dehydration. In DE 198 25 254 an analogous purification method is described in which in addition to water, acetic acid is added to the return stream, whereby a reduction in the ethyl acetate content is achieved. These methods are process stages that are downstream of the synthesis and reduce the formation of by-products through additional measures.

[0011] There is still a need for a method to enable high productivity as well as high selectivity of the catalyst. With regard to selectivity, there is a particular need for methods that suppress the formation of by-products, such as ethyl acetate, that are costly to separate.

5 [0012] The objective of the invention is therefore to overcome the deficiencies in the prior art and to provide synthesis reactor with a catalyst for reducing the formation of by-products when used in a synthesis reactor for producing vinyl acetate, in which gaseous ethylene and acetic acid as well as oxygen or gases containing oxygen undergo a catalytic reaction, and at the same time achieving high selectivity and productivity. Here,
10 productivity is defined as the mass of vinyl acetate formed per mass of catalyst and unit of time expressed in units of $g_{VAM}/kg_{cat} \cdot h$, whereby the calculated mass of the catalyst does not contain a binding agent.

[0013] The device and method according to the invention solve this problem in the prior art in that synthesis reactor with a catalyst is used to produce vinyl acetate by which
15 gaseous ethylene and acetic acid as well as oxygen or gases containing oxygen undergo a catalytic reaction, whereby a wall reactor is used as the synthesis reactor, and the catalyst being a catalyst for use as a wall catalyst in a synthesis reactor for producing vinyl acetate, the synthesis reactor with the catalyst being characterised in that a catalyst is adhesively applied to the wall surfaces of the reaction chambers by way of an oxidic or
20 organic binding agent in a synthesis reactor that is made of stainless steel.

[0014] In an advantageous embodiment of the invention the synthesis reactor is used as a reactor that comprises a number of tubes or stacked plates which have a number of gaps whereby the tubes or gaps can be aligned in any way with regard to each other and ideally run parallel to each other.

25 [0015] It is an advantage if in an optimised embodiment only precisely one dimension of the reaction chambers is less than 2000 μm and preferably less than 1000 μm . In tube-shaped reaction chambers this is the free flow diameter and in gap-type reaction chambers either the height or the width of the gap of the free flow cross-section. The other dimensions, not being of these very small dimensions, have the advantage that
30 seal-tightness, mechanical stresses and manufacturing processes can be more easily controlled. The reaction chambers with the wall catalyst can comprise a number of tubes or gaps arranged by way of plates, whereby these can be aligned in any direction and ideally are parallel to each other.

[0016] The synthesis reactor according to the invention comprises a catalyst which is adhesively applied to the wall surfaces of the reaction chambers by means of a binding agent.

[0016a] In one aspect, there is provided a synthesis reactor with a wall catalyst for producing vinyl acetate, in which gaseous ethylene and acetic acid as well as oxygen or gases containing oxygen undergo a catalytic reaction, the synthesis reactor with the wall catalyst being characterised in that the catalytic synthesis takes place in a number of reaction chambers with the wall catalyst, whereby at least one wall of the reaction chambers is coated with catalyst, and at least one wall of the reaction chambers with the wall catalyst is indirectly cooled, characterised in that the wall catalyst is supported on a powder carrier containing SiO_2 , and the wall catalyst is adhesively applied to the wall surfaces of the reaction chambers by way of an oxidic or organic binding agent in a synthesis reactor that is made of stainless steel.

[0017] Metals can be distributed over the entire catalyst layer, since due to the small layer thickness and the high porosity of the carrier material there are no mass transport resistances during the reaction which have a negative effect on the activity. There is no shell structure as is usual in moulded bodies.

[0018] Advantageously the method according to the invention can be used in explosive process conditions with no restrictions with regard to the optimum operating parameters having to be taken into account because of explosive states being attained. Explosive conditions are taken to mean gas mixtures with a composition which could explode in a defined volume in the conditions present during the process, such as temperature and pressure. Of particular technical relevance is the lower explosion limit for oxygen which in US 3,855,280 is typically quantified at 8%. With the method according to the invention process conditions are covered in which an O_2 content of over 7% by volume is present in the process gas.

[0019] The invention also covers a catalyst for use in a reactor for vinyl acetate synthesis characterised in that the palladium content of the catalyst is 0.5 to 10% by weight, preferably 0.8 to 5% by weight. In another advantageous composition of the catalyst the gold content of the catalyst is 0.25 to 5% by weight, preferably 0.4 to 2.5% by weight. In another advantageous composition of the catalyst according to the invention, the potassium content of the catalyst is 0.5 to 10% by weight and preferably 1 to 4% by weight.

[0020] To test the device according to the invention, the catalyst was prepared in an analogue manner to the preparation in EP 1 008 385 A1 with a powder carrier containing SiO_2 being used identical in composition to the usual bulk catalyst carrier. The catalyst was then applied to two stainless steel plates with webs and activated with potassium acetate. The pairs of plates were connected to each other so that the catalyst layers were opposite each other with a gap of approx. 500 μm being formed. This pair of plates was placed in a pressure-resistant reactor heated by oil and operated almost completely isothermally at 155°C. The temperature increase was less than 1 K whereby measurements were taken at 5 measuring points along the path of flow.

Examples

Example 1

[0021] The pressure in the reactor was in the range of 5 to 9 bars absolute. Ethylene, oxygen, methane and helium were added in gaseous form whereby the methane served as the internal standard for analysis. The acetic acid was added in liquid form and evaporated upstream of the reactor. The gas mixture entering the reactor was composed of the following, expressed in percent by volume: 63.2% ethylene, 5.7% oxygen, 4.2% methane, 9.6% helium and 17.2% acetic acid. Testing was initially started without oxygen, but over the course of one hour the oxygen content can rapidly be increased to the standard content. Analysis was carried out using gas chromatography and a CO₂ detector.

[0022] In an initial test, the results of which are set forth in Table 1, the dependence of the productivity on the palladium and gold content of the catalyst was investigated. The measurements were carried out at 5 bar and at 9 bar as well as with two different gas loads in the catalyst bed. The gas load was measured as product gas volume per mass of catalyst and time using the units l_{VAM}/kg_{cat}*h, whereby only the active catalyst mass was taken into consideration, i.e. without the binding agent proportion. A catalyst prepared according to the above method was used.

Example 1

Pd/Au content in mass %	Productivity [g _{VAM} /kg _{cat} *h] at p = 5 bars and gas load = 12,000 l/kg*h	Productivity [g _{VAM} /kg _{cat} *h] at p = 9 bar and gas load = 24,000 l/kg*h
0.83 / 0.36	450	750
2.50 / 1.10	830	1300
5.00 / 2.20	1120	2100

Table 1: Influence of the noble metal content on productivity

[0023] From Table 1 it can be seen that the productivity increases with increasing Pd/Au content. Although high values are sometimes reported in the prior art as being advantageous in principle, it can be assumed from the lack of appropriate tests or examples that temperatures cannot be controlled in the conventional method with such an active catalyst. An advantage of the invention can be seen here, namely that the

temperature development as a result of a high Pd/Au loading no longer acts as a limit for the method.

Example 2

[0024] In Test 2 the behaviour of the reactor according to the invention was investigated at various gas loads in the catalyst bed.

Gas load in l/kg*h at 5 bar	Productivity in $g_{VAM}/kg_{cat} \cdot h$
3000	300
6000	350
12000	400 - 450 ¹⁾
24000	450 - 480 ¹⁾

Table 2: Influence of the gas load of a Pd/Au wall catalyst (0.83% Pd / 0.36% Au) on productivity

¹⁾ For measurements see also Table

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[0025] From Table 2 it can be seen that an advantage of the invention consists in operating the method at a gas load up to approx. 12,000 l/kg*h. Due to the deviation and disruption-free flow, the pressure loss in the reactor according to the invention is considerably less than in the known tubular reactor which has a catalyst bed. A further increase in the gas load above 12,000 l/kg*h does not bring about a significant increase in productivity.

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Example 3

[0026] Along with the findings from Test 3, in which increasing Pd/Au contents, increasing pressures and increasing gas loads were realised, it can be seen that all these three parameters have a positive effect on productivity, and their variations are not limited by the reactor or the method according to the invention.

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Pd/Au content in mass %	Productivity $[g_{VAM}/kg_{cat} \cdot h]$ pressure 5 bars gas load = 12,000 l/kg*h	Productivity $[g_{VAM}/kg_{cat} \cdot h]$ pressure 5 bars gas load = 24,000 l/kg*h	Productivity $[g_{VAM}/kg_{Kat} \cdot h]$ pressure 9 bars gas load = 24,000 l/kg*h
0.83 / 0.36	450	480	760
2.50 / 1.10	830	850	1350

5.00 / 2.20	1120	not measured	2100
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Table 3: Influence of the operating pressure and the gas load on productivity with different Pd contents

Example 4

[0027] In Test 4 the temperature dependence of the method was investigated whereby the selectivity for vinyl acetate was considered in relation to ethylene and the productivity was considered in relation to vinyl acetate. It was found that with regard to selectivity an optimum is passed, which is in the range of 160°C to 170°C in the case of a pressure of 9 bars and a selected catalyst loading of 0.83% by weight Pd and 0.36% by weight Au, for example, whereby selectivities of almost 98% are achievable. Productivity is also increased with further increases in temperature so that a productivity of up to 1,400 g_{VAM}/kg_{cat}*h was achieved at 185°C at this low Pd/Au loading.

	T = 155°C	T = 165°C	T = 175°C	T = 185°C
VAM Productivity g _{VAM} /kg _{cat} *h	700	900	1150	1400
VAM Selectivity in % (related to C ₂ H ₄)	97.4	97.4	96.8	95.6

Table 4: Influence of the operating temperature at p = 9 bars and gas load = 24,000 l/kg*h
(wall catalyst with 0.83% Pd / 0.36% Au)

Example 5

[0028] In Test 5 an attempt was made to use the method according to the invention under explosive gas conditions by increasing the oxygen concentration. Test conditions 3 and 4 are within the explosive range with regard to O₂/C₂H₄ ratios. An advantage of the invention can be seen in the fact that in order to increase productivity, explosive process conditions can be intentionally set in order to optimise the method.

	Test condition 1	Test condition 2	Test condition 3	Test condition 4
% by volume C ₂ H ₄	63.2	61.2	59.5	57.8
% by volume O ₂	6.0	8.7	11.3	13.8
% by volume HOAc	17.2	16.7	16.2	15.7

Inerts (He, CH ₄)	13.9	13.5	13.1	12.7
Space-time yield VAM g _{VAM} /kg _{cat} *h	430	630	700	1100

Table 5: Effect of increasing the O₂ concentration on the productivity of VAM at p = 5 bars and gas load = 12,000 l/kg*h (wall catalyst with 0.83% Pd / 0.36% Au)

Example 6

- 5 [0029] In Test 6 the influence of the layer thickness on the productivity and area-time yield of vinyl acetate was investigated. The almost constant mass-specific activity of the catalyst at increased layer thickness shows that mass transport resistances play only a subordinate role within the layer. A further advantage of the invention is therefore that there is no need for shell-like noble metal distribution, which is associated with high local
10 noble metal concentrations and thereby low noble metal surface areas.

Layer thickness in µm	Productivity VAM g _{VAM} /kg _{cat} *h	Area-time yield VAM g _{VAM} /m ² _{cat}
300	850	130
500	780	196

Table 6: Influence of the layer thickness of the wall catalyst with 2.5% by mass Pd on the area-time yield of VAM

- 15 [0030] With higher loading of the wall catalyst, a VAM productivity of up to 5 kg_{VAM}/kg_{cat}*h was observed at pressures of up to 9 bars.

Example 7

- [0031] In a further series of tests a Pd/Au catalyst was used which was prepared according to the method described in EP 0 723 810 A1. In contrast to the moulded bodies
20 described in EP 0 723 810 A1 particles with a particle size of 50 – 150 µm were used for the tests described below. The basic material is identical to that of the moulded body. The ethylene concentration in the educt flow was reduced in relation to tests 1 to 6 and replaced with a corresponding volumetric proportion of inert gas and a small proportion of water vapour. Changing the proportion of ethylene in the educt stream to the extent
25 carried out had a negligible influence on the synthesis reaction. In Test 7, the wall catalyst

prepared according to the above method was used, said catalyst containing 2.5% by weight Pd and 1.1% by weight Au. As a further test condition a gas temperature of 155°C and a pressure of 9 bars were set. The composition of the educt gas was selected as follows:

- 5 49.2% by vol. ethylene (C_2H_4)
 18.0% by vol. acetic acid (HOAc)
 1.3 % by vol. water (H_2O)
 31.5% by vol. oxygen and inert gas (helium + methane)

The results of measurement are set forth in Table 7.

O ₂ (%)	Gas load	Productivity	Selectivity VAM (related to C ₂ H ₄)	C ₂ H ₄ conversion
Vol%	l/kg _{cat} *h	g _{VAM} / (kg _{cat} *h)	%	%
6.5	6000	1600	94.3	15.0
9.0	6000	1900	94.7	17.6
11.5	6000	2320	93.6	21.5
14.0	6000	2620	93.4	24.8
14.0	12000	3180	96.0	14.2

Table 7: Influence of the O₂ concentration on productivity and selectivity

- [0032] Test 7 shows that, with a space velocity of 6,000 l/kg_{cat}*h, by increasing the oxygen concentration from 6.5% by volume, which is not in the explosive range, to 14.0% by volume in the explosion range, the conversion of ethylene increases from 15% to 24.8%. In this case it is really surprising that this marked increase in conversion only leads to a very small decrease in selectivity from 94.3 to 93.6%. In actual fact with the very high O₂ concentration in the explosive range, much greater CO₂ formation due to the parallel reaction of ethylene with O₂ is expected here, but surprisingly this did not happen.
- 20 Overall there is an increase in productivity from 1600 g_{VAM}/kg_{cat}*h to 2620 g_{VAM}/kg_{cat}*h.

[0033] With an increase in the space velocity from 6000 to 12,000 l/kg_{cat}*h, the productivity can be increased further to 3180 g_{VAM}/kg_{cat}*h and selectivity with regard to ethylene increases from 93.4 to 96% compared with operation at 6000 l/kg_{cat}*h.

- [0034] Surprisingly it was found that a selectivity of up to approx. 98% could be achieved with regard to ethylene at the same time as very high conversion rates. In addition to this it was surprising to observe that a clearly reduced quantity of by-products was formed. The high vinyl acetate selectivity and the low rate of by-product formation
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consequently result in a considerably reduced need for purification of the product with the method according to the invention in comparison with the method according to the prior art and thus to significant economic advantages.

Claims

1. Synthesis reactor with a wall catalyst for producing vinyl acetate, in which gaseous ethylene and acetic acid as well as oxygen or gases containing oxygen undergo a catalytic reaction, the synthesis reactor with the wall catalyst being characterised in that

- the catalytic synthesis takes place in a number of reaction chambers with the wall catalyst, whereby
- at least one wall of the reaction chambers is coated with catalyst, and
- at least one wall of the reaction chambers with the wall catalyst is indirectly cooled,

characterised in that

- the wall catalyst is supported on a powder carrier containing SiO_2 , and
- the wall catalyst is adhesively applied to the wall surfaces of the reaction chambers by way of an oxidic or organic binding agent in a synthesis reactor that is made of stainless steel.

SYNTHESIS REACTOR WITH A CATALYST FOR THE SYNTHESIS OF VINYL ACETATE IN THE GAS PHASE

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ABSTRACT

The invention relates to a synthesis reactor with a catalyst for the production of monomeric vinyl acetate (VAM), by which gaseous ethylene and gaseous acetic acid as well as oxygen or gases containing oxygen react catalytically, the catalyst being a
10 catalyst for use as a wall catalyst in a synthesis reactor for producing vinyl acetate, the synthesis reactor being characterised in that a catalyst is adhesively applied to the wall surfaces of the reaction chambers by way of an oxidic or organic binding agent in a synthesis reactor that is made of stainless steel.

15 No Suitable Figure.