

## CONTROLLING VINYL ACETATE MONOMER CATALYST DEACTIVATION WITH CARBON DIOXIDE

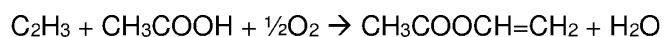
### FIELD OF THE INVENTION

[001] The present invention relates to a process for controlling vinyl acetate monomer catalyst deactivation.

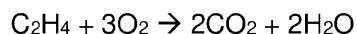
### BACKGROUND OF THE INVENTION

[002] Vinyl acetate, commonly referred to as vinyl acetate monomer or VAM, is a high-volume chemical that is used for the production of several different polymers.

[003] VAM is typically prepared continuously in a gas-phase reaction of ethylene with acetic acid and oxygen.



[004] Carbon dioxide is produced as a byproduct through the oxidation of ethylene.



[005] Because carbon dioxide is considered an unwanted byproduct of the reaction, efforts have been made to decrease the selectivity to carbon dioxide and/or to reduce the amount of carbon dioxide present in the reactor.

[006] U.S. Patent No. 8,029,748 discloses a process for producing VAM in which the selectivity to carbon dioxide is reduced. The process comprises a reactant stream containing high concentrations of reactants in near stoichiometric amounts, The relative amounts of ethylene:acetic acid:oxygen is 2.5:2.5:1.

[007] U.S. Patent No. 7,803,965 discloses a process for producing VAM in which carbon dioxide is removed from the recycle stream to reduce the amount of energy used by the system. The recycle stream is scrubbed to reduce the amount of carbon dioxide to 1 to 4% by volume.

[008] VAM is conventionally prepared in either a fixed bed reactor or a fluidized bed reactor using a catalyst that generally comprises palladium and alkali metal salts on a support material. The catalyst may also contain other elements, such as gold, rhodium

or cadmium. The activity of the catalyst decreases over time. To counter the decrease in catalyst activity, the temperature in the VAM reactor may be increased at the cost of reduced product selectivity. There is a point, however, at which the selectivity of the catalyst decreases and the catalyst must be replaced.

[009] Catalyst deactivation remains a problem in VAM production. Due to deactivation, the catalyst must be replaced periodically, which results in loss of production and extensive costs.

[0010] Motahari et al. (The Canadian Journal of Chemical Engineering, Vol. 94, Issue 3, March 2016, p. 506-511) explored the deactivation of palladium-gold catalyst in VAM production. In the model developed by Motahari et al., the deactivation rate law was determined as a function of time, temperature, and ethylene concentration.

[0011] There remains a need for a process that can reduce catalyst deactivation in VAM production and/or increase the selectivity to VAM.

## **SUMMARY OF THE INVENTION**

[0012] According to one aspect of the present invention, a process for improving catalyst lifetime in the production of vinyl acetate monomer comprises reacting ethylene, acetic acid, and oxygen in the presence of carbon dioxide and a palladium-containing catalyst to produce vinyl acetate monomer. The carbon dioxide is present in an amount ranging from greater than 5 mol% to 20 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide.

## **DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION**

[0013] As used herein, the terms “a,” “an,” “the,” “at least one,” and “one or more” are used interchangeably. The terms “comprises,” “includes,” “contains,” and variations thereof do not have a limiting meaning where these terms appear in the description and claims. Thus, for example, a mixture that includes a polymerization inhibitor can be interpreted to mean that the mixture comprises at least one polymerization inhibitor.

[0014] As used herein, recitations of numerical ranges by endpoints includes all numbers subsumed in that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

For the purposes of the invention, it is to be understood, consistent with what one of ordinary skill in the art would understand, that a numerical range is intended to include and support all possible subranges that are included in that range. For example, the range from 1 to 100 is intended to convey from 1.1 to 100, from 1 to 99.99, from 1.01 to 99.99, from 40 to 6, from 1 to 55, etc.

[0015] As used herein, the recitations of numerical ranges and/or numerical values, including such recitations in the claims, can be read to include the term “about.” In such instances, the term “about” refers to numerical ranges and/or numerical values that are substantially the same as those recited herein.

[0016] Unless stated to the contrary, or implicit from the context, all parts and percentages are based on weight and all test methods are current as of the filing date of this application.

[0017] The present invention relates to a process for improving catalyst lifetime in the production of vinyl acetate monomer.

[0018] The inventors have surprisingly discovered that increasing the amount of carbon dioxide present in the reactor during the production of vinyl acetate monomer results in extending the lifetime of the catalyst by reducing the rate of deactivation of the catalyst. In any process for producing vinyl acetate monomer, the catalyst will lose activity over time. To counter the reduction in activity in conventional vinyl acetate monomer production processes, the temperature in the reactor is increased. Increasing the reactor temperature, however, results in lower selectivity to vinyl acetate monomer. Therefore, decreasing the rate of deactivation is a significant improvement because any decrease in the rate of deactivation results in an increase in the selectivity over the life of the catalyst by enabling the production process to be run at cooler temperatures.

[0019] Vinyl acetate monomer is formed by the acetoxylation of ethylene in a gas phase reaction. Ethylene is reacted with acetic acid and oxygen to form vinyl acetate monomer. In a side reaction, ethylene also reacts with oxygen to form carbon dioxide.

[0020] Through the use of a recurrent neural network model trained with data accumulated from years of running a vinyl acetate monomer production plant, the present inventors have found that including carbon dioxide in the reactor can significantly extend the lifetime (i.e., decrease the rate of deactivation) of the catalyst. The inventors have found that an amount of carbon dioxide ranging from greater than 5 mol% to 20 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide may extend the lifetime of the catalyst by at least 5%, such as by at least 10%. In the production of vinyl acetate monomer, even a 1 or 2% increase in the catalyst lifetime would be significant because catalyst replacement costs substantial amounts of time and money.

[0021] The amount of carbon dioxide entering the reactor is greater than 5 mol%, preferably at least 6 mol%, more preferably at least 8 mol%, even more preferably at least 10 mol%, still more preferably at least 12 mol%, and yet more preferably at least 14 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide entering the reactor. The amount of carbon dioxide entering the reactor is no greater than 20 mol%, preferably no greater than 19 mol%, even more preferably no greater than 18 mol%, and still more preferably no greater than 17 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide entering the reactor. As used herein, the phrase "entering the reactor" means the amount of process gases (i.e., ethylene, acetic acid, oxygen, and carbon dioxide) at the inlet of the reactor. The gases may enter the reactor individually or in combinations of one or more gases.

[0022] Additional gases may also enter the reactor. For example, inert gases or diluents may also be used. The oxygen may be present in the form of oxygen gas or as the oxygen present in air that enters the reactor. Preferably, the oxygen is present in air entering the reactor. When the oxygen is present in air entering the reactor, only the actual amount of oxygen is used to calculate the amounts of the gases.

[0023] The amount of ethylene entering the reactor may range from 20 mol% to 60 mol%, preferably from 25 mol% to 50 mol%, and even more preferably from 30 mol% to

40 mol%, based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide entering the reactor.

[0024] The molar ratio of ethylene to oxygen entering the reactor may range from 8:1 to 2:1. Preferably, the molar ratio of ethylene to oxygen entering the reactor ranges from 7.5:1 to 4:1, and more preferably from 7:1 to 5:1.

[0025] The amount of acetic acid entering the reactor may range from 15 mol% to 55 mol%, preferably from 20 mol% to 45 mol%, and more preferably from 25 mol% to 35 mol%, based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide entering the reactor.

[0026] The molar ratio of acetic acid to oxygen entering the reactor may range from 8:1 to 2:1. Preferably, the molar ratio of acetic acid to oxygen entering the reactor ranges from 7.5:1 to 4:1, and more preferably from 7:1 to 5:1.

[0027] The acetoxylation reactor is preferably operated at above atmospheric pressure, such as, for example above 50psig. The reactor may be maintained at a temperature ranging from 100 °C to 200 °C. The reactor temperature may be changed as the activity of the catalyst changes. For example, when the activity decreases, the temperature of the reactor may be increased to maintain production of the vinyl acetate monomer.

[0028] The reactor may be a fixed bed reactor or a fluidized bed reactor. Preferably, the reactor is a fixed bed reactor.

[0029] The reactor contains a catalyst for the acetoxylation reaction. The catalyst is a palladium-containing catalyst. Preferably, the catalyst contains palladium in an amount of at least 0.5 wt% based on the total weight of the catalyst. More preferably, the catalyst contains palladium in an amount of at least 0.7 wt% based on the total weight of the catalyst.

[0030] The palladium-containing catalyst may contain an additional metal selected from gold, cadmium, and rhodium. Preferably, the palladium-containing catalyst comprises gold. When a gold-palladium catalyst is used, the weight ratio of gold to palladium may

range from 0.01 to 0.8 wt/wt. Preferably, the weight ratio of gold to palladium ranges from 0.1 to 0.7 wt/wt.

[0031] The palladium-containing catalyst may comprise a support. The support may be selected from silica, alumina, and titanium dioxide. Preferably, the support comprises silica. When present, the support may be present in an amount of at least 80 wt% based on the total weight of the catalyst.

[0032] The palladium-containing catalyst may further comprise an alkali metal acetate. Suitable alkali metals include, for example, lithium, sodium, potassium, and cesium. Preferably, the alkali metal acetate comprises potassium acetate. When present, the alkali metal acetate may be present in an amount ranging from 4 wt% to 20 wt% based on the total weight of the catalyst.

#### Example

[0033] The following example illustrates the present invention but is not intended to limit the scope of the invention.

[0034] A recurrent neural network model was trained using MATLAB to model a steady-state, pseudo-homogeneous, plug-flow reactor based on the Hagan Method to describe a single tube of the VAM reactors. The model captured relevant mass and energy balances for describing VAM production and utilized laboratory-based kinetic models to capture VAM kinetics. The neural network was used to evaluate how a range of process variables impacted catalyst deactivation.

[0035] The input layer of the neural network model consisted of a node for each of the process variables listed below in Table 1. In addition, the neural network comprised a hidden layer, and an output layer corresponding to the deactivation rate constants.

Table 1

| <b><i>Symbol</i></b> | <b><i>Description</i></b>            |
|----------------------|--------------------------------------|
| $F_{Acid}$           | Inlet molar flow rate of acetic acid |
| $F_{C_2H_4}$         | Inlet molar flow rate of ethylene    |

|               |                                            |
|---------------|--------------------------------------------|
| $F_{CO_2}$    | Inlet molar flow rate of carbon dioxide    |
| $F_{H_2O}$    | Inlet molar flow rate of water             |
| $F_{N_2}$     | Inlet molar flow rate of nitrogen          |
| $F_{O_2}$     | Inlet molar flow rate of oxygen            |
| $F_{KOAc}$    | Inlet molar flow rate of potassium acetate |
| $T_{inlet}$   | Inlet temperature                          |
| $T_{coolant}$ | Coolant temperature                        |
| $P_{inlet}$   | Inlet pressure                             |
| $\Delta P$    | Pressure drop over axial length of reactor |
| $t_{down}$    | Time since reactor last down               |

[0036] To avoid vanishing gradients caused when older information in a time series is forgotten by the model, a long short-term memory recurrent neural network was used. The neural network was trained using hourly averages collected from a VAM production plant over a period of 576 days. 80% of the available data was used to train the model, with the additional 20% of data being used to test the fit of the model. The overall normalized root mean square errors for the training and test data was 0.4643 and 0.4986, respectively.

[0037] Using the model described above, it was surprisingly discovered that increasing the flow rate of carbon dioxide entering the reactor by 5% resulted in a 14% increase in the amount of VAM over the perturbation period, i.e., the deactivation rate of the catalyst was significantly improved.

We claim:

1. A process for improving catalyst lifetime in the production of vinyl acetate monomer, the process comprising:  
  
reacting ethylene, acetic acid, and oxygen in the presence of carbon dioxide and a palladium-containing catalyst to produce vinyl acetate monomer,  
  
wherein the carbon dioxide is present in an amount ranging from greater than 5 mol% to 20 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide.
2. The process of claim 1, wherein the carbon dioxide is present in an amount ranging from 8 mol% to 19 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide.
3. The process of claim 2, wherein the carbon dioxide is present in an amount ranging from 10 mol% to 18 mol% based on the total amount of ethylene, acetic acid, oxygen, and carbon dioxide.
4. The process of any one of the preceding claims, wherein the catalyst comprises palladium and gold.
5. The process of claim 4, wherein the ratio of gold to palladium ranges from 0.01 to 0.8 wt/wt.

6. The process of claim 5, wherein the ratio of gold to palladium ranges from 0.1 to 0.7 wt/wt.

7. The process of any one of the preceding claims, wherein the amount of palladium in the catalyst is at least 0.5 wt% based on the total weight of the catalyst.

8. The process of claim 7, wherein the amount of palladium in the catalyst is at least 0.7 wt% based on the total weight of the catalyst.

9. The process of any one of the preceding claims, wherein the catalyst comprises a support selected from silica, alumina, titanium dioxide, and magnesium oxide.

10. The process of claim 9, wherein the support comprises silica.

11. A process of claim 9 or claim 10, wherein the support is present in an amount of at least 80% based on the total weight of the catalyst.

12. The process of any one of the preceding claims, wherein the catalyst comprises an alkali metal acetate in an amount ranging from 4 to 20 wt% based on the total weight of the catalyst.

13. The process of claim 12, wherein the alkali metal acetate comprises an alkali metal selected from lithium, sodium, potassium, and cesium.

14. The process of claim 13, wherein the alkali metal acetate comprises potassium acetate.