a 10-membered ring and having at least 5% of its cation exchange capacity occupied by one or more alkali metal cations.

As described above methyl acetate may be hydrolysed to acetic acid in the presence of acid zeolite catalysts and other solid Brønsted acid catalysts. Methyl acetate feedstock may be derived from processes for the carbonylation of ethers or may be supplied as a mixture with methanol as a byproduct from the hydrolysis of polyvinyl acetate to produce polyvinyl alcohol. In such processes, acetaldehyde and its precursor compounds, such as 1,1 dimethoxyethane, may be formed as unwanted by-products, generally as a result of side-reactions.

US 2009/0107833 describes a method of removing acetaldehyde from ternary mixtures of methyl acetate, methanol and acetaldehyde which includes a) feeding the mixture to a distillation column; b) distilling the mixture at a pressure of 10 psig or more to generate an overhead vapour stream enriched in acetaldehyde as compared with the feed mixture and a residue stream depleted in acetaldehyde as compared with the feed mixture; and c) withdrawing the residue stream deleted in acetaldehyde from the distillation column.

WO 2009/045253 describes a method for removing aldehyde impurities from a methyl acetate supply by reacting the supply with a polyol and converting the aldehyde impurities to cyclic acetals which can subsequently be removed by distillation.

Summary

In an aspect, there is provided a process for the hydrolysis of a methyl acetate feed with at least one of water and methanol in the presence of at least one Brønsted acid catalyst to produce acetic acid in which process the performance of the catalyst is improved by using as a feed to the process a methyl acetate feed in which the total amount of acetaldehyde and 1,1 dimethoxyethane impurities is maintained at 100 ppm wt or less calculated as mass equivalents of acetaldehyde.

In another aspect, there is provided a process for the dehydration-hydrolysis of methyl acetate and methanol to co-produce acetic acid and dimethyl ether which process is integrated with a carbonylation process for the production of methyl acetate which integrated process comprises the steps : a) carbonylating dimethyl ether with a carbon monoxide-containing gas in the presence of a zeolite carbonylation catalyst to produce a carbonylation reaction product and recovering methyl acetate therefrom; b) pre-treating at

least a portion of the methyl acetate recovered in step (a) to reduce the amount of acetaldehyde and 1,1 dimethoxyethane impurities therein; c) converting methanol and methyl acetate by dehydration-hydrolysis in the presence of at least one Brønsted acid catalyst to co-produce acetic acid and dimethyl ether; in which dehydration-hydrolysis process the performance of the catalyst is improved by using as a methyl acetate feed methyl acetate pre-treated in step (b) in which the total amount of acetaldehyde and 1,1 dimethoxyethane impurities is maintained at 100 ppm wt or less calculated as mass equivalents of acetaldehyde.

Detailed Description

It has now been found that the presence of acetaldehyde and its precursor compounds in solid acid catalysed processes for the production of acetic acid can have a deleterious effect on the catalytic performance (activity and/or lifetime) of the catalysts and, in particular on the performance of solid Brønsted acid catalysts, such as zeolites employed in such processes. The performance of these catalysts can be considerably improved by controlling the amount of acetaldehyde and its precursor compounds present in methyl acetate feedstocks to such processes. In particular, it has been found that by maintaining acetaldehyde and its precursor compounds in a total amount of up to about 100 ppm wt calculated as mass equivalents of acetaldehyde is particularly beneficial to catalyst lifetime.

Specific acetaldehyde precursor compounds found to be detrimental include the acetal, 1,1-dimethoxyethane. This acetal compound in the presence of solid Brønsted acid catalysts and methanol is a source of acetaldehyde and vice-versa via the equilibrium

Claims:

1. A process for the hydrolysis of a methyl acetate feed with at least one of water and methanol in the presence of at least one Brønsted acid catalyst to produce acetic acid in which process the performance of the catalyst is improved by using as a feed to the process a methyl acetate feed in which the total amount of acetaldehyde and 1,1 dimethoxyethane impurities is maintained at 100 ppm wt or less calculated as mass equivalents of acetaldehyde.

2. A process according to claim 1 wherein the methyl acetate feed is derived from processes for carbonylating of dimethyl ether with a carbon monoxide-containing gas in the presence of a zeolite carbonylation catalyst.

3. A process for the dehydration-hydrolysis of methyl acetate and methanol to co-produce acetic acid and dimethyl ether which process is integrated with a carbonylation process for the production of methyl acetate which integrated process comprises the steps :

a) carbonylating dimethyl ether with a carbon monoxide-containing gas in the presence of a zeolite carbonylation catalyst to produce a carbonylation reaction product and recovering methyl acetate therefrom;

b) pre-treating at least a portion of the methyl acetate recovered in step (a) to reduce the amount of acetaldehyde and 1,1 dimethoxyethane impurities therein;

c) converting methanol and methyl acetate by dehydration-hydrolysis in the presence of at least one Brønsted acid catalyst to co-produce acetic acid and dimethyl ether;

in which dehydration-hydrolysis process the performance of the catalyst is improved by using as a methyl acetate feed methyl acetate pre-treated in step (b) in which the total amount of acetaldehyde and 1,1 dimethoxyethane impurities is maintained at 100 ppm wt or less calculated as mass equivalents of acetaldehyde.

~~4. A process according to any one of claims 1 to 3 wherein the total amount of impurities present in the methyl acetate feed is maintained at 0 to 50 ppm wt calculated as mass equivalents of acetaldehyde.~~

~~5. A process according to claim 4 wherein the total amount of impurities in the feed is maintained at 0 to 25 ppm wt calculated as mass equivalents of acetaldehyde.~~

~~6~~4. A process according to any one of claims 1 to ~~5~~3 wherein the methyl acetate feed comprises 50 to 99 mol% methyl acetate, >0 to 45 mol% dimethyl ether and a total amount of acetaldehyde and 1,1 dimethoxyethane impurities of more than 100 ppm wt up to 1 wt%

calculated as mass equivalents of acetaldehyde.

~~7~~5. A process according to any one of claims 1 to ~~6~~4 wherein the methyl acetate feed is pre-treated to reduce the amount of impurities to less than 100 ppm wt calculated as mass equivalents of acetaldehyde.

~~8. A process according to claim 7 wherein the methyl acetate feed is pre-treated to reduce the amount of impurities to 50 ppm wt or less calculated as mass equivalents of acetaldehyde.~~

~~9~~6. A process according to claim ~~7 or claim 8~~5 wherein the methyl acetate feed is pre-treated by a fractional distillation method.

~~10~~7. A process according to ~~any one of claims 7 to 9~~claim 5 or claim 6 wherein methyl acetate comprising >0 to 80 mol% methyl acetate, a total amount of more than 100 ppm up to 1 wt% of acetaldehyde and 1,1 dimethoxyethane impurities and >0 to 50 mol% dimethyl ether is pre-treated to provide a methyl acetate feed having a total acetaldehyde and 1,1 dimethoxyethane impurity content of 0 to 100 ppm wt.

~~11~~8. A process according to claim ~~10~~7 wherein the methyl acetate to be pre-treated further comprises one or more of acetic acid, water, carbon oxides and hydrogen.

~~12~~9. A process according to any one of claims 1 to ~~11~~8 wherein the Brønsted acid catalyst is a zeolite.

~~13~~10. A process according to claim ~~12~~9 wherein the zeolite comprises at least one channel having a 10-membered ring.

~~14~~11. A process according to claim ~~12~~9 or claim ~~13~~10 wherein the zeolite has a framework type selected from FER and MFI.

~~15~~12. A process according to claim ~~14~~11 wherein the zeolite has framework type FER and is selected from one or both of ferrierite and ZSM-35.

~~16~~13. A process according to any one of claims ~~12~~9 to ~~15~~12 wherein the zeolite is in an exchanged form with one or more alkali metal cations.

~~17~~14. A method according to ~~any one of claims 1 to 16~~claim 9 wherein the Brønsted acid catalyst is a heteropolyacid.

~~18~~15. A process according to any one of claims 1 to ~~17~~14 wherein the methyl acetate feed further comprises one or both of methanol and water.

~~19~~16. A process according to claim ~~18~~15 wherein the methyl acetate feed further comprises ~~methanol and water.~~

~~20. A process according to claim 18 or claim 19 wherein the methyl acetate feed further comprises~~ one or more of carbon oxides, hydrogen and acetic acid.

~~21. A process according to any one of claims 1 to 20 wherein methanol is supplied to the process as a separate feed thereto.~~

~~22~~17. A process according to any one of claims 3 to ~~21~~ 16 wherein the dehydration-hydrolysis process is carried out as a vapour phase process.

~~23~~18. A process according to any one of claims 1 to ~~22~~ 17 wherein the process is carried out at a temperature of from 100 to 350 °C.

~~24~~19. A process according to claim ~~23~~18 wherein the process is carried out at a temperature of 180 to 280 °C.

~~25~~20. A process according to any one of claims 2 to ~~24~~19 wherein the zeolite carbonylation catalyst comprises a zeolite which comprises at least one channel defined by an 8-membered ring.

~~26. A process according to any one of claims 1 to 25 wherein the process is operated as a continuous process.~~