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(54) **Title**: PROCESSES FOR MAKING METHACRYLIC ACID

(57) **Abstract**: Processes are described for making methacrylic acid via methacrolein from a biobased isobutene, wherein the biobased isobutene is prepared from ethanol or from acetic acid in the presence of a $Zn_xZr_yO_z$ mixed oxide catalyst, the biobased isobutene is oxidized to methacrolein and the methacrolein is further oxidized to methacrylic acid.

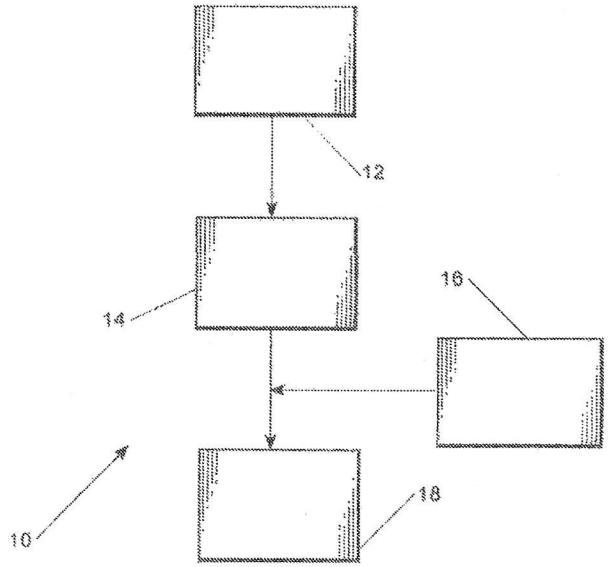

Fig. 1

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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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— *with international search report (Art. 21(3))*

PROCESSES FOR MAKING METHACRYLIC ACID

Field of the Invention

[0001] The present application concerns processes for making methacrylic acid via methacrolein from isobutene.

Background Art

[0002] In this regard, isobutene is widely used for the production of a variety of industrially important products, and has been used to make methacrylic acid via methacrolein in one commercially known route. Isobutene has however been produced commercially to date through the catalytic or steam cracking of fossil feedstocks. As fossil resources are depleted and/or become more costly to use, renewable source-based routes to isobutene are increasingly needed – especially in consideration of increased demand for isobutene.

[0003] A hard-template method has previously been described for synthesizing $Zn_xZr_yO_z$ mixed oxides for the direct and high yield conversion of ethanol (from the fermentation of carbohydrates from renewable source materials, including biomass) to isobutene, wherein ZnO was added to ZrO_2 to selectively passivate zirconia's strong Lewis acidic sites and weaken Brönsted acidic sites while simultaneously introducing basicity. The objectives of the hard template method were to suppress ethanol dehydration and acetone polymerization, while enabling a surface basic site-catalyzed ethanol dehydrogenation to acetaldehyde, an acetaldehyde to acetone conversion via aldol-condensation/dehydrogenation, and a Brönsted and Lewis acidic/basic site-catalyzed acetone-to-isobutene reaction pathway.

[0004] High isobutene yields were in fact realized, but unfortunately, as later experienced by Mizuno et al. (Mizuno et al., "One –path and Selective Conversion of Ethanol to Propene on Scandium-modified Indium Oxide Catalysts", *Chem. Lett.*, vol. 41, pp. 892-894 (2012)) in their efforts to produce propylene from ethanol, it was found that further improvements in the catalyst's stability were needed.

Summary Of The Invention

[0005] Our United States Patent Application Ser. No. 61/720,433 (the " '433 application"), filed October 31, 2012 for "Stable Mixed Oxide Catalysts for Direct Conversion of Ethanol to Isobutene and Process for Making" , concerns the discovery that these improvements could be realized without adding modifying metals and without a reduction in the initial high activity (100 percent ethanol conversion) that had been observed in these mixed oxide catalysts. The '433 application thus in sum concerns an improved stability, longer lifetime catalyst for converting ethanol to isobutene.

[0006] Separately, we discovered that acetic acid, rather than ethanol, may be converted to a biobased isobutene product using certain mixed oxide catalysts, including a mixed oxide catalyst as made in the '433 application. This discovery became the basis for United States Patent Application Ser. No. 61/737,312 (the " '312 application"), filed December 14, 2012 for "Process and Catalyst for Conversion of Acetic Acid to Isobutene".

[0007] Building on these discoveries, the present invention in one aspect concerns a process for making methacrylic acid via methacrolein from a biobased isobutene, wherein the biobased isobutene is prepared from ethanol in the presence of a $Zn_xZr_yO_z$ mixed oxide catalyst, the biobased isobutene is oxidized to methacrolein and the methacrolein is oxidized to methacrylic acid.

[0008] In certain embodiments according to this first aspect, the $Zn_xZr_yO_z$ mixed oxide catalyst exhibits improved stability for the conversion, exhibiting less than 10 percent loss, more preferably less than 5 percent loss and still more preferably less than 2 percent loss in isobutene selectivity over a period of 200 hours on stream. In other embodiments, the $Zn_xZr_yO_z$ mixed oxide catalyst is made by a process as described in the '433 application, broadly comprising forming a solution of one or more Zn compounds, combining one or more zirconium-containing solids with the solution of one or more Zn compounds, drying the wetted solids, then calcining the dried solids.

[0009] In a second, related aspect, the present invention concerns a process for making methacrylic acid via methacrolein from a biobased isobutene, wherein the biobased isobutene is prepared from acetic acid in the

presence of a catalyst, the biobased isobutene is oxidized to methacrolein and the methacrolein is oxidized to methacrylic acid. In certain embodiments, the catalyst is a $Zn_xZr_yO_z$ mixed oxide catalyst, especially a catalyst made by a process as described in the '433 application, and the process of making the starting biobased isobutene is carried out as described in the '312 application.

Brief Description Of The Drawings

[0010] Figure 1 schematically depicts a process for producing a wholly biobased methacrylic acid from a wholly biobased isobutene made from ethanol in the presence of a $Zn_xZr_yO_z$ mixed oxide catalyst, especially such a catalyst made by a process as described in the '433 application.

[0011] Figure 2 schematically depicts a process for producing a biobased methacrylic acid, particularly a wholly biobased methacrylic acid, from a biobased and especially a wholly biobased isobutene made from acetic acid, according to the second aspect of the present invention as summarized above.

Description Of Embodiments

[0012] Referring now to Figure 1, a process 10 is schematically illustrated wherein ethanol 12 is converted to isobutene 14 in the presence of a catalyst, particularly, a $Zn_xZr_yO_z$ mixed oxide catalyst. The isobutene 14 is then combined with oxygen from an oxygen source 16 and oxidized to yield methacrolein, which is then oxidized with oxygen from oxygen source 16 to provide a methacrylic acid product 18.

[0013] The ethanol 12 is conventionally derived from biological carbon sources, for example, by fermentation of five- and especially six-carbon sugars, so that the isobutene 14 and subsequent methacrylic acid product 18 are desirably wholly-biobased.

[0014] Parenthetically, by "biobased", we mean those materials whose carbon content is shown by ASTM D6866 to be derived from or based in significant part (at least 20 percent or more) upon biological products or renewable agricultural materials (including but not being limited to plant, animal and marine materials) or forestry materials. "Wholly biobased" thus will be understood as referring to materials whose carbon content by ASTM D6866 is entirely or substantially entirely (for example, 95 percent or more) indicated as of biological origin.

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