Title: PROCESS FOR MAKING BIOBASED ISOPRENE

Abstract: Processes are described for making biobased isoprene, wherein a biobased isobutene prepared from acetic acid in the presence of a catalyst is combined with a formaldehyde source to form a reaction mixture, and the reaction mixture is reacted to yield biobased isoprene. In certain embodiments, methyl-tert-butyl ether prepared by reacting the same biobased isobutene with methanol serves as a formaldehyde source, being oxidatively cracked to produce formaldehyde as well as isobutene for being converted to the biobased isoprene.

Declarations under Rule 4.17:

— as to applicant’s entitlement to apply for and be granted a patent (Rule 4.17(h))
— as to the applicant’s entitlement to claim the priority of the earlier application (Rule 4.17(hi))

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PROCESS FOR MAKING BIOBASED ISOPRENE

Technical Field

[0001] Our United States Patent Application Ser. No. 81/720433 (the "'433 application"), filed October 31, 2012 for "Stable Mixed Oxide Catalysts for Direct Conversion of Ethanol to Isobutene and Process for Making", concerns an improved stability, longer lifetime catalyst for converting ethanol to isobutene, while our 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", concerns the discovery 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. Our subsequent United States Patent Application Ser. No. 81/838,188 (the "'188 application"), filed June 18, 2013 for "Process for Making Biobased Fuel Additives", concerns the manufacture of alkyl-t-buty ether useful as antiknock additives for gasoline, for example, methyl-tet-buty ether (MTBE) and ethyl-tert-buty ether (ETBE), from a biobased isobutene product made according to neither the '433 or '312 applications. As isoprene may be made from isobutene or from MTBE, the present application concerns the further refinement of making biobased isoprene from biobased isobutene prepared as described in either or both of the '433 and '312 applications or from MTBE prepared as described in the '188 application.

Background Art

[0002] As background, conventionally isoprene has been recovered from pyrolysis gasoline in naphtha cracking to produce ethylene, by a series of fairly capital intensive steps, initially cyclopentadiene is removed from the pyrolysis gasoline by dimerization and distillation. Subsequently, plpyrolylenes are separated out by superfractionation, and the isoprene (at 10 to 2.0% of the pyrolysis gasoline) is then recovered by extractive distillation using a solvent. In recent years, however, with the availability of abundant, inexpensive natural gas, ethylene has increasingly been produced using lighter feedstocks for the steam crackers so that pyrolysis gasoline production has declined.
A number of other petroleum processing-based or --dependent
routes to isoprene have been developed as well. As summarized in WO
2012/038247 A1 by Vermelren et al., "Production of Isoprene from Iso-
Butanol" ("WO '247"), isoprene can be produced by the Isolation of
isoamylenes from refinery and petroleum cuts and the subsequent
hydrogenation of the isoamylenes over an iron oxide catalyst promoted with
potassium compounds. Isoprene can also be produced from isopentane by
a double dehydrogenation. In another known process, isoprene is produced
by a Prins condensation of a C_4 olefin feed with an aldehyde, typically
formaldehyde, with the C_4 olefin feed commonly including isobutene or one or
more isobutene precursors such as an alkyl-t-butyl ether under conditions
which will provide isobutene. The isobutene reacts with formaldehyde to give
4,4-dimethyl-m-dioxane which decomposes to provide the desired isoprene
product.

WO '247 reports a number of examples of processes of this
general character. For example, US 4,511,751 describes a process wherein
isobutene and tertiary butanol and a formaldehyde source are fed, together
with water, into an acidic aqueous solution continuously or intermittently while
maintaining the reaction pressure in an adequate range and at the same time
distilling off the isoprene product and unreacted starting materials, together
with water, from the reaction zone. US 4,593,145 is cited for describing a
process for producing isoprene, characterized in that an alkyl-t-butyI ether
(e.g., methyl-t-buty! ether (fVITBE) or ethyl-t-buty! ether (ETBE) as are still
commercially manufactured and extensively used as antiknock fuel additives)
and a formaldehyde source are fed, together with water, into an acidic
aqueous solution continuously or intermittently while maintaining the reaction pressure in an adequate range and at the same time distilling off the product
isoprene, unreacted starting materials, isobutene and tertiary butanol,
together with wafer, from the reaction zone. Other cited examples include EP

It is also known to produce isoprene from tertiary alkyl ethers
(such as MTBE) and an oxygen source by a catalytic process. For example,
in US 3,574,78G isoprene is produced by passing a mixture of fVITBE and air
over a mixed oxide catalyst, cracking the \( \text{MTBE} \) to isobutene and methanol, oxidizing the methanol to formaldehyde and then reacting the isobutene and formaldehyde to produce isoprene. Other references supply isobutene and methanol separately. The methanol is oxidized to formaldehyde alongside methanol generated from the cracking of MTBE, and the formaldehyde so formed reacts with the supplied isobutene plus that Isobutene generated from the cracking of \( \text{MTBE} \). Still other references supply isobutene and methanol directly rather than generating the same by cracking \( \text{MTBE} \), oxidizing the methanol to formaldehyde with an oxygen source in the presence of an oxidation catalyst and then reacting the formaldehyde thus formed with the isobutene feed.

[0008] While there are thus a number of known methods for producing isoprene, each of these methods has shared the disadvantage of being dependent at least to some extent on petroleum-based or \( \text{-derived} \) materials and on petroleum processing economics.

[0007] In recognition of the desirability of a renewable source-derived isoprene, the \( \text{WO'247} \) application provides a process for making isoprene using isobutanol, especially isobutanol produced using biomass as a primary feedstock, as an isobutene precursor. More particularly, at least 25 mole percent of the carbon implicated in the isobutanol is obtained from renewable resources, whether by the base-catalyzed Guerbet condensation of methanol with ethanol and/or propanol, by hydrogenation of synthesis gas from the gasification of biomass and/or by an amino acid biosynthetic route from carbohydrates from biomass. The at least partly bioderived isobutanol in turn provides at least 10 up to 100 percent of the isobutene, with the balance being provided by t-butanol, another isobutene precursor such as MTBE or from fresh isobutene.
Summary Of The Invention

[0008] As mentioned previously, since our '433 and '312 applications provide means by which a biobased isobutene may be viably produced, in one aspect the present invention concerns a process for making isoprene wherein a biobased isobutene prepared as described in either of these applications is combined with a formaldehyde source to form a reaction mixture, and the reaction mixture is reacted to provide a product mixture, then isoprene is recovered from the product mixture. In a preferred embodiment, the reaction mixture is reacted while distilling away a mixture comprising produced isoprene, water, unreacted starting materials and other low boiling components.

[0000] Since MTBE may also be used to produce isoprene according to certain conventionally known processes, in another aspect the present invention concerns a process for making isoprene wherein MTBE produced from a biobased isobutene in the manner of the '188 application is cracked to provide isobutene and methanol, methanol from the MTBE is oxidized to provide a source of formaldehyde, and the formaldehyde and isobutene are combined to form a reaction mixture. The reaction mixture is reacted to provide a product mixture, then isoprene is recovered from the reaction mixture. Again, in a preferred embodiment, the reaction mixture is reacted while distilling away a mixture comprising produced isoprene, water, unreacted starting materials and other low boiling components.

[0010] In yet another aspect, the present invention concerns a process wherein both biobased isobutene and MTBE prepared from biobased isobutene are combined with a formaldehyde source to form a reaction mixture, and the reaction mixture is reacted to provide a product mixture, then isoprene is recovered from the product mixture. In a preferred embodiment, the reaction mixture is reacted while distilling away a mixture comprising produced isoprene, water, unreacted starting materials and other low boiling components.

[0011] In yet another aspect, wholly biobased butyl rubber is provided by copolymerizing biobased isobutene prepared as described in either of the
433 and '312 applications with biobased isoprene prepared using additional
of the same biobased isobutene and a wholly biobased formaldehyde source
and/or using a wholly biobased MTBE prepared in the manner of the '188
application.

**Brief Description Of The Drawings**

[0 0 12] Fig11uure1 1  sscshhheemmeeaaammattticcccaaillffyy ddeepppicccittts a pprroocceessss ffooor mmmaakkkiinnngg iissoopprreennee

[[00011331]] Fig11uure2 2  sscshhheemmeeaaammattticcccaaillffyy ddeepppicccittts a pprroocceessss ffooor mmmaakkkiinnngg iissoopprreennee

[[00011144]] Fig11uure3 3  sscshhheemmeeaaammattticcccaaillffyy ddeepppicccittts a pprroocceessss cccoommbbiinnnniinnngg tthhee

[[00001111]] Fig11uure4 4  sscshhheemmeeaaammattticcccaaillffyy ddeepppicccittts a pprroocceessss ffooor mmmaakkkiinnngg a wwhhhoollllyy

[[00001111]] Fig11uure5 5  sscshhheemmeeaaammattticcccaaillffyy ddeepppicccittts a pprroocceessss ffooor mmmaakkkiinnngg ffoorr

**Description Of Embodiments**

[00117] Referring now to Figure 1, a process embodiment 10 according
to a first aspect is schematically illustrated wherein acetic acid 12 is converted
to isobutene 14 in the presence of a catalyst, particularly, a $Zn\{\cdot\}O\{\cdot\}_r$ mixed
oxide catalyst, and the isobutene 14 is then reacted with formaldehyde 1$\theta$ to
produce an isoprene product 18.

[0018] Where the methanol 20 from which the formaldehyde 18 is
obtained (by oxidation according to any of the commercially-practiced or
known methods) is wholly biobased in origin, being derived from biological
carbon sources rather than from methane from natural gas, for example, a
wholly biobased isoprene 18 may be obtained.

[0019] Parenthetically, by "biobased", we mean those materials whose
carbon content is shown by A S T M D8886 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 D8868 is entirely or substantially entirely (for example, 95 percent or more) indicated as of biological origin.

[0020] In this respect ASTM Method D8886, similar to radiocarbon dating, compares how much of a decaying carbon isotope remains in a sample to how much would be in the same sample if it were made of entirely recently grown materials. The percentage is called the biobased content of the product. Samples are combusted in a quartz sample tube and the gaseous combustion products are transferred to a borosilicate break seal tube. In one method, liquid scintillation is used to count the relative amounts of carbon isotopes in the carbon dioxide in the gaseous combustion products. In a second method, 13C/12C and 14C/12C isotope ratios are counted (14C) and measured (13C/12C) using accelerator mass spectrometry. Zero percent 14C indicates the entire lack of 14C atoms in a material, thus indicating a fossil (for example, petroleum based) carbon source. One hundred percent 14C, after correction for the post-1950 bomb injection of 14C into the atmosphere, indicates a modern carbon source. ASTM D6866 effectively distinguishes between biobased materials and petroleum derived materials in part because isotopic fractionation due to physiological processes, such as, for example, carbon dioxide transport within plants during photosynthesis, leads to specific isotopic ratios in natural or biobased compounds. By contrast, the 13C/12C carbon isotopic ratio of petroleum and petroleum derived products is different from the isotopic ratios in natural or bioderived compounds due to different chemical processes and isotopic fractionation during the generation of petroleum, in addition, radioactive decay of the unstable 14C carbon radioisotope leads to different isotope ratios in biobased products compared to petroleum products.

[0021] Acetic acid 12 can be obtained by various methods from a number of starling materials, which in turn permits a number of integrated processes to be considered for producing the isoprene 18 with improved
utilization of renewable resources. An example is schematically shown in Figure 5, discussed more fully below.

[0022] For example, acetic acid can be produced from a source of five and six carbon sugars 2.2 by fermentation. US 8,509,180 and US 8,252,567 seek to improve upon known processes for making ethanol and butanol/hexanol, respectively, by means including the fermentation of five and six carbon sugars into acetic acid. In US 6,509,180, the acetic acid is esterified to form an acetate ester which may then be hydrogenated (using hydrogen from, e.g., steam reforming of natural gas, electrolysis of water, gasification of biomass or partial oxidation of hydrocarbons generally) to ethanol. In US 8,252,587, the ethanol formed in this manner can be used to make butanol and hexanol, by subjecting the ethanol with acetate, acetic acid or mixtures thereof to an acidogenic fermentation using, for example, species of the bacteria Clostridium (Clostridium kluyveri is mentioned), to produce butyrate, butyric acid, caproate, caproic acid or mixtures thereof. These materials then in turn are acidified to convert butyrate and caproate to butyric acid and caproic acid, the butyric and caproic acids are esterified and then the butyric and caproic acid esters undergo reduction by hydrogenation, hydrogenolysis or reduction by carbon monoxide to provide butanol and ethanol.

[0023] As related in these two patents and as is well known to those skilled in the fermentation art, the fermentation of five and six carbon sugars to form acetic acid can be accomplished by various organisms. More particularly, homoacetogenic microorganisms are able through fermentation to produce acetic acid with 100% carbon yield; these microorganisms internally convert carbon dioxide to acetate, in contrast to a process for producing ethanol from sugars obtained from biomass, wherein carbon dioxide is produced as a byproduct.

[0024] Examples of homoacetogens given by US 8,252,687 are microorganisms of the genus Moorella and Clostridium, especially microorganisms of the species Moorella thermoaceicum (described as formerly classified as Clostridium thermoaceficum) or Clostridium formicoaceticum. US 8,252,567 represents that about one hundred known
acetogens in twenty-two genera were known as of 2009, and cross-
review of acetogenic microorganisms.

[0025] Other references describing fermentation methods for producing
acetic acid from five and six carbon sugars include US 4,935, 380; US
8,236,534; US 4,513,084; US 4,371,619 and US 4,508,012; both one-step
fermentation processes from the sugars to acetic acid, acetates or both are
disclosed, as well as two-step processes involving a first fermentation to lactic
acid (by iactobacius or known methods of homoiacotic fermentation,
preferably) followed by a second fermentation to convert lactic acid to acetic
acid, for example, using Clostridium formicQaeticum.

[0026] Any of the known fermentation methods may, in short, he used
to produce acetic acid 12 for conversion to isobutene 14 as shown in Fig. 1,
but homoace!ogenic fermentation methods are considered preferable in that
carbon dioxide is not produced as a byproduct – the carbon dioxide
represents a yield loss from the overall process to make isobutene and as a
greenhouse gas is undesirable particularly in the context of a process to make
a needed product more sustainably from renewable resources.

[0027] As well or in the alternative, the acetic acid feedstock 12 can be
made from ethanol 24, according to any of several known methods employing
oxidative fermentation with acetic acid bacteria of the genus Ac&tohactetet.

[0028] As well or in the alternative, the acetic acid feedstock 12 can be
made from methanol 20, through combination with carbon monoxide
according to the most industrially used route for making acetic acid, for
example, in the presence of a catalyst under conditions effective for the
carbonylation of methanol. A variety of carbonylation catalysts are known in
this regard, see, for example, US 5,672,743; US 5,728, 871 ; US 5,773,642;

[0029] The wholly biobased isobutene 14 enabled by the process of the ‘312 application and formaldehyde 16 may be reacted as schematically
shown in Figure 1 to produce Isoprene 18 according to any of a number of
known methods, including but not limited to those methods summarized
above and described more fully in the WO’247 application; US 4,511,751 ; US
4,593,145; EP 108323; EP 1614671; EP 2157072; GB 1370899; US
3,972,955 and the various prior isoprene manufacturing methods summarized
in each of these. Again, using methanol 20 derived from biological carbon
sources to prepare the formaldehyde 16, a wholly biobased isoprene 18 is
enabled.

[0030] In this regard, with increasing concerns for the abatement of
greenhouse gases such as carbon dioxide in recent years, a substantial
amount of work has been reported on methods to convert carbon dioxide to
methanol, see, for example, Wesselbaum et al., "Hydrogenation of Carbon
Dioxide b Methanol by Using a Homogeneous Ruthenium-Phosphine
Short Review of Catalysis for CO₂ Conversion", Catalysis Today, vol. 148, pp
221-231 (2009); Borodko et al., "Catalytic Hydrogenation of Carbon Oxides –
a 10-Year Perspective", Applied Catalysis A: General, vol. 188, pp 355-362
(1999); and US 8,212,088 to Olah et al., "Efficient and Selective Chemical
Recycling of Carbon Dioxide to Methanol, Dimethyl Ether and Derived
Products" and the various additional references cited in each of these. Those
skilled in the art will thus be well-acquainted with processes and associated
catalysts for producing methanol 20 from carbon dioxide, carbon monoxide
and hydrogen variously obtained from the anaerobic digestion of biomass
through methane, from electrolysis of water using energy from geothermal
sources, by electrolytic cleavage of carbon dioxide to produce carbon
monoxide and water and so forth.

[0031] Turning now to Figure 2, a process embodiment 26 is
schematically shown for making isoprene 28 from a biobased methylethyl-butyl
ether (MTBE) 30 according to a second aspect of the present invention. It
should be noted, parenthetically, that for avoiding possible confusion different
reference numbers are employed in Figure 2 as opposed to Figure 1, though
for example the isoprene 28 is desirably substantially the same as isoprene
18 in the process 10 of Figure 1, being of the same essential quality,
character and functionality as isoprene obtained from conventional petroleum-
based processing. The biobased MTBE 30 can be combined with air and
converted to isoprene as described in US 3,574,780, through passing a
mixture of MTBE 30 and air over a mixed oxide catalyst, cracking the MTBE 30 to isobutene and methanol oxidizing the methanol to formaldehyde and then reacting the isobutene and formaldehyde to produce the isoprene 28.

[0032] The biohased MTBE 30 in turn is produced by a process as described in the ’188 application, from isobutene 32 produced from acetic acid 34 produced as described in the ’312 application (using a catalyst, particularly a Zn,Zr,O mixed oxide catalyst, and especially a Zn,Zr,O mixed oxide catalyst made as described in the ’433 application) and from methanol 36.

[0033] In alternative embodiments not specifically illustrated in the schematic, those skilled in the art will appreciate that additional methanol 38 (beyond that used to form the MTBE 30 and produced therefrom as described in US 3,574,780) and additional isobutene 32 can be supplied alongside the MTBE 30 to make the isoprene 28. As well, isobutene 32 and methanol 38 can be supplied directly for oxidation and without a separate step of forming the MTBE 30; the methanol is oxidized to formaldehyde with an oxygen source in the presence of an oxidation catalyst, and the formaldehyde is then reacted with the isobutene feed preferably using the same catalyst to produce the isoprene 28.

[0034] In a still further process embodiment schematically shown in Figure 3, a process 38 is shown in which acetic acid 40 is converted to isobutene 42 as described in the ’312 application. A portion of the isobutene 42 is combined with a corresponding portion of methanol 44 to produce MTBE 48, and at least a portion of the MTBE 48 is converted to isoprene 48 by cracking the MTBE to isobutene and methanol, oxidizing the methanol to formaldehyde and causing the isobutene and formaldehyde to react to form the desired isoprene. The isobutene and formaldehyde thus derived are supplemented in the process 38 by additional isobutene 42 and by formaldehyde 50 separately produced from additional methanol 44 according to known processes.

[0035] Turning now to Figure 4, because wholly biobased isobutene can be made as described in the ’312 application and wholly biobased isoprene made by a process as described herein (the processes schematically shown in Figures 1-3 being examples), a wholly biobased butyl
rubber can be made. Processes for the copolymerization of isobutene and isoprene are well known and have been commercially practiced for years, though some recent examples of published patent applications am/i/or patents for processes for making such copolymers include EP 1215241 B1, EP 1449850A1, EP 1426387B1, US 7,041760 and US 7,851,577. For purposes of the present invention, any known process for copolymerizing isobutene and isoprene may be used, however.

[0036] In the process embodiment 52 schematically shown in Figure 4, acetic acid 54 (whether obtained by fermentation of five and/or six-carbon sugars 58, from ethanol 58 by oxidative fermentation, from methanol 80 by carbonylation or a combination of these, all as described above) is converted b wholly biobased isobutene 62 by a process as described in the ‘312 application and summarized below. Wholly biobased isoprene 64 is prepared from formaldehyde 66, with the formaldehyde 68 in turn being prepared by oxidizing a portion of the methanol 80, through cracking of MTSE 68 prepared from wholly biobased isobutene according to the ‘188 application or by a combination of these synthetic methods as previously described. The wholly biobased isobutene 82 and wholly biobased isoprene 64 are then copolymerized to provide a wholly biobased butyl rubber product 70 using any of the known processes for accomplishing the copolymerization.

[0037] Turning now finally to Figure 5, a non-limiting example 72 is shown of an integrated process for making biobased alternatives to one or more of the valuable products isobutene, Isoprene, MTBE and ETBE which have all heretofore been made at least in part through petroleum processing, through use of the core acetic acid to isobutene conversion described in the ‘312 application. While one example 72 is detailed herein, those skilled in the art and familiar with the known processes for producing methanol, ethanol and acetic acid (some of which have been mentioned above or will be mentioned below) and with the known methods by which the "building block" gases carbon dioxide, carbon monoxide and hydrogen may be generated and used to make one or more of the same methanol, ethanol and acetic acid feeds will undoubtedly be able to conceive of a number of other integrated process schemes which all make use of the core acetic acid to isobutene
conversion, but differ in the precise manner or extent to which carbon dioxide, carbon monoxide and hydrogen gases are optimally used.

[0038] Nevertheless, in the particular integrated process embodiment 72 shown schematically in Figure 5, biomass 74 can be a source of five and six carbon sugars 78, which can undergo a fermentation step 78 as earlier mentioned to make acetic acid 80. Some of the sugars can be fermented according to known methods for fermentation of five- and six-carbon sugars to make ethanol 82, with the ethanol 82 in turn being useful for making ETBE 84 by conventionally practiced etherification process technology and/or for making acetic acid 80 as described above. Carbon dioxide generated as a byproduct in the ethanol fermentation can variously be used as suggested by stream 86 in a homoaetogenic fermentation 78 for making the acetic acid 80, or can be used as suggested by stream 88 to make methanol 90. This carbon dioxide (that is, in streams 86 and 88) can be combined for either or both purposes with carbon dioxide from a variety of other sources, for example, with carbon dioxide captured from industrial emissions, generated in the combustion of fossil fuels, sequestered in underground reservoirs or contained in biosynthesis gas 92 from the combustion, gasification or partial oxidation of biomass 74 or of a non-fermentable biomass fraction generated in a fractionation of the biomass 74 to produce fermentable sugars 78. In the context of a biomass fractionation process as described in any of several commonly-assigned, copending applications, namely, published applications WO 2011/097065 and WQ 2011/097075 both to Binder et al., as well as Patent Cooperation Treaty Applications Ser. No. FCT/US2012/2/056593, filed Sept. 21, 2012 for “C1-C2 Organic Acid treatment of Lignin Biomass to Produce Acyliated Celluliosio Pulp, Hemi cellulios, Lignin and Sugars and Fermentation of the Sugars”, and PCT/US2012/058593, filed April 10, 2013 for "Liquid-Liquid Separation of Lignocellulosic Biomass to Produce Sugar-Syrups and Lignin Fractions", the non-fermentable biomass fraction would include lignin.

[0039] The methanol 90 can variously be combined with biobased isobutene 94 (from acetic acid 80) for forming the MTBE fuel additive 96, combined with carbon monoxide 98 from biosynthesis gas 92 (or from the
electrolytic cleavage of CQ₂ from any of the sources mentioned above in connection with the generation of the methanol 90) to produce acetic acid 80 and/or used to make formaldehyde 100, with the latter being useful for combining with isobutene 94 to make isoprene 102. The isoprene 102 and ssobutene 94 can then be used to make a butyl rubber product 104, if desired. As well, where demand for MT8E is not as strong as demand for isobutene, for isoprene and/or for butyl rubber or other polymer products that may be conventionally made using the isobutene and isoprene, MTBE S4 can be oxidatively cracked to produce additional of the formaldehyde 100 and isobutene 04.

[0040] The acetic acid so is converted to isobutene 94 as taught in the '312. application, preferably using a Zn, Zr, O₃ mixed oxide catalyst. In one embodiment, the Zn, Zr, O₃ mixed oxide catalyst can be made by a "hard template" or "confined space synthesis" method generally of the character used by Jacobsen et al., "Mesoporous Zeolite Single Crystals", Journal of the American Chemical Society, vol. 122, pp. 7116-7117 (2000), wherein nanozeolites were prepared.

[0041] More particularly, the same carbon black (BP 2000, Cabot Corp.) may be used as a hard template for the synthesis of nano-sized Zn, Zr, O₃ mixed oxides, rather than nanozeolites as in Jacobsen et al. Prior to use, the BP 2000 template is dried, for example, at 180 °C overnight. Calculated amounts of zirconyl nitrate hydrate (Sigma-Aldrich, greater than 99.8% purity) and Zn(N0₃)₂·6H₂O (Sigma-Aldrich, greater than 99.8% purity) are dissolved in a given amount of water, and sonicated for 15 minutes to produce a clear solution with desired concentrations of Zn and Zr. In one preparation, about 25 grams of the obtained solution are then mixed with 8.0 grams of the preheated BP 2000 to achieve incipient wetness, and the mixture is transferred to a ceramic crucible and calcined at 400 degrees Celsius for 4 hours, followed by ramping the temperature to 550 degrees Celsius (at a ramp rate of 3 degrees Celsius/minute) and holding at 550 degrees Celsius for another 20 hours. Nanosized white powders are obtained, having a mean particle size of less than 10 nanometers.
The nanosized Zn\textsubscript{x}Zr\textsubscript{y}O\textsubscript{z} mixed oxide catalysts made by a hard template method are further described by Sun et al., in "Direct Conversion of Bio-ethanol to isobutene on Nanosized Zn\textsubscript{x}Zr\textsubscript{y}O\textsubscript{z} Mixed Oxides with Balanced Acid-Base Sites", Journal of the American Chemical Society, vol. 133, pp 11098-11099 (2011), along with findings related to the character of the mixed oxide catalysts formed thereby and the performance of the catalysts for the ethanol to isobutene conversion, given certain Zn/Zr ratios, residence times and reaction temperatures.

Alternatively, the Zn\textsubscript{x}Zr\textsubscript{y}O\textsubscript{z} mixed oxide catalysts may be made as described in the 433 application, by a process broadly comprising, in certain embodiments, 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 so that the solution wets the zirconium-containing solids to a state of incipient wetness, drying the wetted solids, then calcining the dried solids. In other embodiments, a solution is formed of one or more Zr compounds, the solution is combined with one or more Zn-containing solids so that the solution wets the Zn-containing solids to a state of incipient wetness, the wetted solids are dried and then the dried solids are calcined.

In certain embodiments, the Zn\textsuperscript{+}Zr\textsubscript{y}O\textsubscript{z} mixed oxide catalysts (whether made by the hard template or incipient wetness methods) are characterized by a Zn/Zr ratio (x:y) of from 1:100 to 10:1, preferably from 1:30 to 1:1, especially 1:20 to 1:5, and still more preferably 1:12 to 1:10.

Parenthetically, in the present application where any range of values is given for any aspect or feature of the mixed oxide catalysts or any process described for using the mixed oxide catalysts, the given ranges will be understood as disclosing and describing all subranges of values included within the broader range. Thus, for example, the range of 1:100 to 10:1 will be understood as disclosing and describing not only the specific preferred and more preferred subranges given above, but also every other subrange including a value for x between 1 and 10 and every other subrange including a value for y between 1 and 100.

The catalysts made by the alternative, incipient wetness method are consistent in their particle size with the catalysts described in the
Jaecbsen et al. article, namely, composing aggregates of less than 10 nnv sized particles with a highly crystalline structure. The Zn oxide component is again highly dispersed on the Zr oxide component.

In certain embodiments, the Zn$_x$Zr$_y$O$_z$ mixed oxide catalysts are characterized as low sulfur catalysts, containing less than 0.14 percent by weight of sulfur. In the '433 application, it was reported in this regard that catalysts made by the incipient wetness method would desirably be substantially sulfur-free, preferably including less than 0.01 percent by weight of sulfur and more preferably including less than 0.001 weight percent of sulfur. It was postulated that the reduced sulfur content enabled by the incipient wetness method as compared to the hard template method contributed significantly to the much improved stability observed for the incipient wetness method catalysts of the '433 application for the ethanol to isobutene process.

In the context of a process for converting acetic acid to isobutene, however, as mentioned in the '312 application, in at least some embodiments and under certain process conditions some sulfur does appear to be beneficial, though as just indicated, it is expected that the amount of sulfur will preferably be such that the catalysts are characterized as low sulfur catalysts. Such low sulfur catalysts are most readily made by the incipient wetness method described briefly above and in greater detail in the '433 application.

In principle, provided the zinc and zirconium compounds and solids in these embodiments have a sufficiently low sulfur content in order to produce a low sulfur content when combined according to the incipient wetness method, any combination of zinc and zirconium materials and any solvent can be used that will permit the zinc and zirconium components to mix homogeneously whereby, through incipient wetness impregnation, one of the zinc or zirconium components are well dispersed on a solid of the other component for subsequent drying and conversion to the oxide forms through calcining. As exemplified in the '312 application, low sulfur catalysts can also be made by the incipient wetness method starting with zinc and zirconium compounds that are sulfur-free or substantially sulfur-free, then doping in a
desired sulfur content into the Zn₉Zr₉O₂₇ mixed oxide catalysts used in certain embodiments of the acetic acid to isobutene process of the '312 application.

[0050] The conditions and times for the drying and calcining steps of an incipient wetness preparation will depend, of course, on the particular zinc and zirconium materials and solvent used, but in general terms, the drying step can be accomplished in a temperature range of from 80 degrees Celsius to 200 degrees Celsius over at least 3 hours, while the calcination can take place at a temperature of from 300 degrees Celsius to 1500 degrees Celsius, but more preferably a temperature of from 400 to 800 degrees Celsius is used. The calcination time can be from 10 minutes to 48 hours, with from 2 to 10 hours being preferred.

[0051] In still other embodiments, low sulfur catalysts as described could be prepared by a hard template method as described in the Jacobsen et al. publication, except that a suitably very low sulfur content carbon is used for the hard template to realize a low sulfur content in the finished catalyst.

[0052] In certain embodiments described in the '312 application, the acetic acid to isobutene process can be conducted continuously in the gas phase, using a fixed bed reactor or flow bed reactor. The reaction temperature may be in a range from 350 to 700 degrees Celsius, preferably, in a range from 400 to 500 degrees Celsius, and the WHSV can be in a range from 0.01 hr⁻¹ to 10 hr⁻¹, preferably from 0.05 hr⁻¹ to 2 hr⁻¹. Acetic acid/water solutions with steam to carbon ratios from 0 to 20, preferably from 2 to 5 can be used to provide acetic acid to the catalyst. An inert carrier gas, such as nitrogen, can be used.

[0053] The production of the more stable mixed oxide catalysts of the '433 application and the use of mixed oxide catalysts to convert both of ethanol and acetic acid to isobutene are demonstrated for purposes of illustration in the following non-limiting examples:

[0054] Example 1

[0055] Commercial zirconium hydroxide was dried at 120 degrees Celsius for more than 5 hours. Calculated amounts of Zn(NO₃)₂ (from Sigma-Aldrich, more than 99.8 percent purity) were dissolved in water to form a series of clear solutions. Dried zirconium hydroxide (also from Sigma-Aldrich,
more than 99.8 percent purity) was then mixed with the solutions in turn by incipient wetness, in order to form wet powders impregnated with Zn in certain proportions to the zirconium in the form of the dried zirconium hydroxide powder. The wetted powders were then dried at 80 degrees Celsius for 4 hours, followed by calcination at 400 degrees Celsius for 2 hours and at 800 degrees Celsius for 3 hours to obtain a series of Zn*Zf₂O₆ catalysts.

[0058] Ethanol to isobutene runs were conducted with the catalysts thus prepared in a fixed-bed stainless steel reactor, having an inside diameter of 5 millimeters. A given amount of catalyst was packed between quartz wool beds. A thermocouple was placed in the middle of the catalyst bed to monitor the reaction temperatures. Before beginning the reaction, the catalyst beds were first pretreated by flowing 50 ml/minute of nitrogen at 450 degrees Celsius through the catalyst over a half hour, then a mixture of ethanol/water at steam to carbon ratios from 1 to 5 was introduced into an evaporator at 180 degrees Celsius by means of a syringe pump and carried into the reactor by the flowing nitrogen carrier gas. Meanwhile, the product line was heated to in excess of 150 degrees Celsius before a cold trap, to avoid condensing the liquid products in the product line.

[0057] A Shimadzu 2400 gas chromatograph equipped with an auto sampling valve, HP-Plot Q column (30 m, 0.53 mm, 40 pm) and flame ionization detector was connected to the line between the reactor outlet and cold trap to collect and analyze the products in the effluent gas. After the cold trap, an online micro-GC (MicroGC 3000A equipped with molecular sieves 5A, plot U columns and thermal conductivity detectors) was used to analyze the product gases specifically, using nitrogen as a reference gas.

[0058] An ethanol/water solution (steam to carbon ratio of 2.5) was then supplied by flowing N₂ to the reactor at a weight hourly space velocity (WHSV) of 0.95 hr⁻¹. The ethanol concentration was 15.1 percent by weight, and the reaction temperature was 450 degrees Celsius. Ethanol conversion was 100% throughout, and isobutene selectivity declined by less than 2 percent over 200 hours on stream for the series of catalysts prepared as described.
Thermogravimetric and differential scanning calorimetry analysis of the recovered, spent catalysts showed only about 0.7 weight percent of coke after 207 hours onstream.

Example 2

Commercial zirconium hydroxide was dried at 120 degrees Celsius for more than 5 hours. A calculated amount of Zn(NO₃)₂ (from Sigma-Aldrich, more than 99.8 percent purity) was dissolved in water, forming a clear solution. The dried zirconium hydroxide (which was also from Sigma-Aldrich, more than 99.8 percent purity) was then mixed with the solution by incipient wetness, in order to form wet powders impregnated with Zn. The wetted powder was then dried at 80 degrees Celsius for 4 hours, followed by calcination at 550 degrees Celsius for 3 hours, to obtain a Zn₁Zr₆O₂ catalyst.

An acetic acid to isobutene process was conducted with the catalyst thus prepared in a fixed-bed stainless steel reactor having an inside diameter of 5 millimeters. 100 mg of the catalyst was packed between quartz wool beds. A thermocouple was placed in the middle of the catalyst bed to monitor the reaction temperature. Before beginning the reaction, the catalyst bed was pretreated by flowing 50 ml/minute of nitrogen at 450 degrees Celsius through the catalyst over a half hour. A 25 weight percent solution of acetic acid in water was then introduced into an evaporator at 180 degrees Celsius by means of a syringe pump, and the vaporized steam/acetic acid was carried into the reactor by a flowing nitrogen carrier gas at an acetic acid concentration in the gas phase of 1.36 weight percent and a WHSV of 0.1 grams of acetic acid per gram of catalyst per hour. Meanwhile, the product line was heated to in excess of 150 degrees Celsius before a cold trap, to avoid condensing the liquid products in the product line. A reaction temperature of 415 degrees Celsius was employed.

A Shimadzu 2400 gas chromatograph equipped with an auto sampling valve, HP-Plot Q column (30 m, 0.53 mm, 40 µm) and flame ionization detector was connected to the line between the reactor outlet and cold trap to collect and analyze the products in the effluent gas. After the cold trap, an online micro-GC (MicroGC 3000A equipped with molecular sieves 5A,
plot U columns and thermal conductivity detectors) was used to analyze the product gases specifically, using nitrogen as a reference gas.

A consistent product of about 5 percent by weight of methane, about 10 percent by weight of acetone, about 33 percent by weight of carbon dioxide and more than about 50 percent by weight of the desired isobutene product was obtained; in contrast to the ethanol to isobutene process using these same \( \text{Zn}_x\text{Zr}_y\text{O}_z \) mixed oxide catalysts in Example 1, no ethylene or propylene was produced. The catalyst showed very high stability over the full duration of the run, with no signs of observable deactivation after more than 1400 minutes of time-on-stream operation.

Examples 3 through 31

A number of additional catalysts were prepared by first drying commercial zirconium hydroxide at 120 degrees Celsius for more than 5 hours. Calculated amounts of \( \text{Zn}(\text{N}0_{3})_2 \) (from Sigma-Aldrich, more than 99.8 percent purity) were dissolved in wafer to form a series of clear solutions. The dried zirconium hydroxide (also from Sigma-Aldrich, more than 99.8 percent purity) was then mixed with the solutions in turn by incipient wetness, in order to form wet powders impregnated with \( \text{Zn} \) in certain proportions to the zirconium in the form of the dried zirconium hydroxide powder. The wetted powders were then dried at 80 degrees Celsius for 4 hours, followed by calcination at the temperature indicated in Table 1 below for 3 hours, to obtain a series of \( \text{Zn}_x\text{Zr}_y\text{O}_z \) catalysts by an Incipient wetness method. These catalysts were used to convert ethanol to isobutene in the manner of Example 1. Particular reaction conditions, whether the reaction temperature, WHSV or steam to carbon ratio, for example, were varied to compare the effect on the selectivities to acetone and isobutene at full conversion of the ethanol. For several of the catalysts, some amount of sulfur was purposely doped into the catalyst to assess the effect of sulfur at those certain levels on the selectivities to acetone and to isobutene. Thus, the catalyst for example 28 was doped with 10 ppm of sulfur, while for example 29 the catalyst was doped with 50 ppm of sulfur and for example 30 with 200 ppm (by weight).
Table 1 - Additional Ethanol to Isobutene Runs

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<th>WHSV (g&lt;sub&gt;ethanol&lt;/sub&gt;/g&lt;sub&gt;catalyst&lt;/sub&gt;hr)</th>
<th>Steam to carbon ratio</th>
<th>Ethanol (gas wt %)</th>
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For these additional examples of converting acetic acid to isobutene, additional $\text{Zn}_x\text{Zr}_y\text{O}_z$ mixed oxide catalysts were prepared both by the incipient wetness method (IW in Table 2 below) but also by the prior art hard template method (HI), and these were evaluated and the products analyzed using the same apparatus and method described above but under different sets of reaction conditions (as summarized in Table 2 below).
Table 2 – Further Acetic acid to isobutene Examples

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<tr>
<th>Ex#</th>
<th>Catalyst</th>
<th>Zn/Zr ratio</th>
<th>Reaction temp. (°C)</th>
<th>WHSV ($\text{H}<em>2\text{O}$$</em>\text{mol}$/($\text{H}_2\text{O}+\text{Zr}$))</th>
<th>Steam to carbon ratio</th>
<th>$C_{\text{acetic acid}}$ (wt%)</th>
<th>Acetone selectivity (wt%)</th>
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CLAIMS:
1. Wholly biobased isoprene.
2. Wholly biobased butyl rubber.
3. A process for making Isoprene, comprising;
   converting acetic acid to isobutene in the presence of a catalyst;
   and
   reacting the isobutene with formaldehyde.
4. A process comprising copolymerizing isobutene made from acetic acid in the presence of a catalyst and isoprene prepared according to claim 3.
5. A process according to claim 3, wherein the acetic acid is obtained at least in part by fermentation of one or more of the five- and six- carbon sugars.
6. A process according to claim 3, wherein the acetic acid is obtained at least in part through an oxidative fermentation from ethanol.
7. A process according to claim 3, wherein the acetic acid is obtained at least in part by carbonylation of methanol.
8. A process according to claim 7, further comprising combining carbon dioxide and hydrogen under conditions which are effective for making at least a portion of the methanol which is carbonylated to make acetic acid.
9. A process according to either of claims 3 or 8, further comprising combining carbon dioxide and hydrogen under conditions which are effective for making methanol, and oxidizing the methanol so formed to provide at least a portion of the formaldehyde that is reacted with the isobutene.
10. A process as in claim 3, wherein the catalyst for converting the acetic acid to isobutene is a Zn, Zr, O mixed oxide catalyst.
11. A process as in claim 10, wherein the catalyst contains less than 0.14 percent by weight of sulfur.
12. A process as in claim 11, wherein the catalyst contains less than 0.01 percent by weight of sulfur.
13. A process as in claim 12, wherein the catalyst contains less than 0.001 percent by weight of sulfur.
14. A process for making isoprene, comprising;

- converting acetic acid to isobutene in the presence of a catalyst;
- reacting the isobutene with methanol to form biobased MTBE;
- oxidatively cracking at least a portion of the biobased MTBE from acetic acid to produce isobutene and formaldehyde; and
- reacting the isobutene and formaldehyde to form biobased isoprene.
A. CLASSIFICATION OF SUBJECT MATTER
C07C II/18(2006.01)i, C07C II/09(2006.01)i, B01J 23/06(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07C I/18; C07C I/24; C12P I/00; C07C 5/09; C07C 63/06; C08F 226/06; C07C 11/09; B01J 23/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
eKOMPASS/KIPO internal) & Keywords : biobased isoprene, butyl rubber, acetic acid, isobutene, formaldehyde, carbon dioxide, hydrogen, oxide catalyst, methanol, MTBE, methyl-tert-butyl ether

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>US 2010-0216958 Al (PETERS, MATTHEW W. et al.) 26 August 2010 See abstract and claims 1-43</td>
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<td>US 2011-0172475 Al (PETERS, MATTHEW W. et al.) 14 July 2011 See abstract and claims 1-57</td>
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<td>US 4,511,751 A (NINAGAWA, YOICHI et al.) 16 April 1985 See abstract and claims 1-13</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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