Process for preparing metal and mixed metal oxide catalysts

Abstract

Methods of preparing a catalyst including yttrium, zirconium, or a combination thereof are provided to improve the active site density and reactivity of Lewis Acid Base pairs on the surface of the catalysts. The method includes mixing a zirconium-containing precursor, an yttrium-containing precursor or a combination thereof with a precipitant to obtain a mixture; heating the mixture, and adding an organic molecule to the mixture. The method further includes separating solids from the mixture, wherein the solids are the catalyst and the catalyst comprises yttrium, zirconium or a combination thereof.

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Claims

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What is claimed is:

1. A method of preparing a metal oxide catalyst comprising: mixing a zirconium containing precursor, an yttrium containing precursor or a combination thereof with a precipitant to obtain a mixture; heating the mixture; adding a surfactant comprising an organic molecule to the mixture; and separating solids from the mixture; wherein the solids are the catalyst, wherein the catalyst comprises zirconium, yttrium, or a combination thereof.

2. The method of claim 1, wherein the catalyst comprises yttrium.

3. The method of claim 1, wherein the catalyst comprises zirconium.

4. The method of claim 1, wherein the catalyst comprises yttrium and zirconium having a molar ratio of 1 : 50 to 50: 1.

5. The method of any one of the preceding claims, further comprising washing the solids with a hydroxide, water, or a combination thereof.

6. The method of any one of the preceding claims, further comprising drying the solids.

7. The method of any one of the preceding claims, further comprising calcining the solids.

8. The method of claim 5, wherein the hydroxide comprises ammonium hydroxide, sodium hydroxide, or a combination thereof.

9. The method of claim 5, wherein the hydroxide is a solution having a pH of about 7 to 10, or about 9.

10. The method of any one of the preceding claims, wherein the heating is carried out a temperature in a range from about 50°C to about 250°C, for about 1 hour to about 24 hours.

11. The method of any one of the preceding claims, wherein the organic molecule comprises a carboxylic acid, or a carboxylate anion.

12. The method of claim 11, wherein the carboxylic acid comprises lauric acid, or its laureate form.

13. The method of claim 6, wherein the dr ing is carried out at a temperature of about 25°C to about 110°C.

14. The method of claim 7, wherein the calcining is carried out at a temperature of about 300°C to about 800°C. for about 2 hours to about 12 hours.

15. The method of claim 1, wherein the catalyst comprises yttrium in an amount of about 0.3% to about 80%, based on total weight of the catalyst.

16. The method of claim 1 , wherein the catalyst comprises yttrium oxide in an amount of about 1 wt% to about 99 wt%, based on total weight of the catalyst.

17. The method of claim 1. wherein the catalyst comprises zirconium in an amount of about 0.5% to about 70%, based on total weight of the catalyst.

18. The method of claim 1, wherein the catalyst comprises zirconium oxide in an amount of about 1 wt% to about 99 wt%, based on total weight of the catalyst.

19. The method of any one of the preceding claims, wherein the yttrium containing precursor comprises yttrium nitrate, yttrium chloride, yttrium acetate, yttrium oxalate, yttrium hydroxide, yttrium organophosphate, yttrium alkoxide, yttrium carbonate, yttrium hydroxycarbonate, yttrium carboxylate, yttrium acetyl acetonate. yttrium, yttrium oxide, or a combination thereof.

20. The method of any one of the preceding claims, wherein the zirconium containing precursor comprises zirconium oxide, zirconium oxynitrate, zirconium chloride, zirconium acetate, zirconium oxalate, zirconium hydroxide, zirconium organophosphate, zirconium alkoxide, zirconium carbonate, zirconium hydroxy carbonate, zirconium carboxylate, zirconium acetylacetonate, zirconium, zirconium hydroxide, or a combination thereof.

21. The method of any one of the preceding claims, wherein the yttrium containing precursor, the zirconium containing precursor or combination thereof is mixed with water or alcohol.

22. The method of claim 4, wherein the molar ratio of yttrium to zirconium is about 0.05 to about 50.

23. The method of any one of the preceding claims, wherein the catalyst has a BET surface area of about 20 m^2/g to about 250 m^2/g.

24. The method of any one of the preceding claims, wherein the catalyst is a metal oxide catalyst.

25. The method of claim 24, wherein the metal oxide catalyst has a surface with an M-0 site of the Lewis type and of balanced acid-base strength, wherein M comprises yttrium or zirconium.

26. The method of any one of the preceding claims, further comprising cleaning a surface of the catalyst with a surface cleaning reagent.

27. The method of claim 26, wherein the surface cleaning reagent comprises dimethyl ether, ethylene, propylene, methanol, /e/7-butyl alcohol, methyl tert-butyl ether, di-tert-butyl ether, anisole, dimethyl carbonate, or combinations thereof.

28. The method of claim 26, wherein the surface cleaning reagent comprises dimethyl ether.

29. The method of claim 26. wherein the cleaning of the surface removes excess water or CO2 through the surface cleaning reagent reacting with the water or CO2 species bound at the oxide surface.

30. The method of any one of claims 1-25. further comprising cleaning a surface of the catalyst by heating the catalyst at a temperature of about 300°C to about 800°C.

31. The method of claim 30, wherein the cleaning does not include applying a surface cleaning reagent.

32. The method of claim 30, wherein the cleaning further comprises applying a surface cleaning reagent.

33. A catalyst composition comprising the catalyst prepared according to the method of any one of claims 1-32.

34. A method of performing a reaction using a catalyst composition of claim 33, wherein the reaction comprises alkane dehydrogenation, alkene hydrogenation, alkene dehydrogenation, olefin-paraffin alkylation, from CO/H2 mixtures without O-rej ection as H2O or CO2, C-C bond formation via alkene oligomerization or metathesis, dehydrocyclization (alkanes/alkenes to arenes), dehydrocyclodimerization (alkanes/alkenes to arenes with a larger number of C-atoms), transfer hydrogenation, hydroformylation/carbonylation. aromatization, dearomatization, reforming, isomerization, and bifunctional reactions in which one of the aforementioned functions can be combined with a Bronsted acid function.

35. The method of claim 34, wherein the reaction comprises alkane dehydrogenation.

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Description

PROCESS FOR PREPARING METAL AND MIXED METAL OXIDE CATALYSTS

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PROCESS FOR PREPARING METAL AND MIXED METAL OXIDE CATALYSTS

CROSS REFERENCE TO RELATED APPLICATION(S)

[0001] The present invention claims priority to U.S. Provisional Application No. 63/635.767 filed on April 18, 2024, the entire contents of which are incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] Disclosed herein are methods of preparing a catalyst. The method includes preparing a catalyst including yttrium or its oxide form, zirconium or its oxide form, or a combination thereof.

BACKGROUND

[0003] In the chemical industry', propene is an important intermediate for the production of a variety of compounds. For example, propene is used in the production of propylene oxide, acrylonitrile, cumene, acrylic acid, C3 and higher alcohols, or polypropylene. Historically, propene has been available primarily as a co-product from steam crackers and an off-gas product from fluid catalytic cracking units in oil refineries. These technologies have been found to be insufficient to meet the persistent growth in the market demand for propene, leading to the development of new technologies, such as dehydrogenation of propane.

[0004] Thus, dehydrogenation technologies and catalysts have been extensively developed and commercialized in recent years. Among them, the propane dehydrogenation (PDH) has been one of the most common alternate technologies because of its standalone suitability. Nonlimiting representative PDH technologies include those employing platinum group metal (PGM) catalysts (e.g., Linde-BASF, Oleflex, STAR, and FCDh (DOW) processes), or Cr- containing catalysts (e.g., Catofin and FDB-4 processes). In recent years, alternate catalytic materials have been explored to address the toxicity' and environmental hostility' of Cr-based systems and/or to reduce or replace the high costs of PGM catalysts.

[0005] Metal oxides, such as ZrO_2, are promising alternative catalyst compositions for heterolytic catalytic reactions (including alkane dehydrogenation) because of the presence of Lewis acid-base (LAB) pairs that catalyze dehydrogenation reactions. A major limitation in the use of metal oxides for PDH is their fast deactivation. During the dehydrogenation of hydrocarbons such as propane, the acid-base pairs of metal oxide dehydrogenation catalysts (including ZrCh) may be deactivated by (i) titration of active sites by H_2O and/or CO_2, which directly derive from the gas feed streams or are formed indirectly via reactions of O_2 or oxygenate impurities from gas streams with propane and/or H_2; and/or (ii) coke deposition resulting from the adsorption of paraffin-derived molecules on M-0 sites and their further transformations; and/or (iii) sintering and/or annealing of the catalyst particles and active sites due to exposure to high temperatures. In addition, due to facile reactions of reductants with lattice O-atoms, some metal oxide dehydrogenation catalysts, e g., CeCh, TiCh and MoO_x, can be reduced to a lower oxidation state or even the metallic state over time, potentially resulting in activation or deactivation, either through intrinsic loss of active sites, loss of site competence, or from one of the above mechanisms.

[0006] Efforts have been made to develop regeneration/reactivation processes for these catalysts. For example, metal oxide catalysts with surfaces rendered at least partially inactive by bound CO_2 and/or H_2O may be activated and/or reactivated using high temperature thermal regeneration processes. However, the loss of activity some catalysts undergo due to sintering and annealing during the thermal regeneration process is not recoverable and performance deteriorates with successive regeneration cycles.

[0007] Accordingly, there is a need for a method of preparing a thermally stable catalyst including yttrium or its oxides, zirconium or its oxides, or a combination thereof, that can be used for dehydrogenation/hydrogenation reactions, or other reactions thereof.

SUMMARY

[0008] In some embodiments, a method of preparing a metal oxide catalyst is provided. The method includes mixing a zirconium-containing precursor, an yttrium-containing precursor, or a combination thereof with a precipitant to obtain a mixture: heating the mixture; adding a surfactant comprising an organic molecule to the mixture; and separating solids from the mixture. The method further includes wherein the solids are the catalyst, wherein the catalyst comprises zirconium, yttrium, or a combination thereof.

[0009] In some embodiments, the metal oxide/mixed metal oxide cataly st may include yttrium. In some embodiments, the metal oxide/mixed metal oxide catalyst may include zirconium.

[00010] In some embodiments, the metal oxide/mixed metal oxide catalyst may include yttrium and zirconium having a molar ratio of 1 :50 to 50: 1 of yttrium to zirconium.

[00011] In some embodiments, the method may further include washing the solids with a hydroxide, water, or a combination thereof. In some embodiments, the hydroxide may include ammonium hydroxide, sodium hydroxide, or a combination thereof. In some embodiments, the hydroxide may be a solution having a pH of about 7 to 10, or about 9.

[00012] In some embodiments, the method may further include drying the solids. In some embodiments, the drying may be carried out at a temperature of about 25°C to about 110°C.

[00013] In some embodiments, the method may further include calcining the solids. In some embodiments, the calcining is carried out at a temperature of about 300°C to about 800°C, for about 2 hours to about 12 hours.

[00014] In some embodiments, the heating may be carried out at a temperature in a range from about 50°C to about 250°C, for about 1 hour to about 24 hours.

[00015] In some embodiments, the organic molecule may include a carboxylic acid, or a carboxylate anion. In some embodiments, the carboxylic acid may include lauric acid, or its laureate form.

[00016] In some embodiments, the catalyst may include yttrium in an amount of about 0.3% to about 80%, based on total weight of the catalyst. In some embodiments, the catalyst may include yttrium oxide in an amount of about 1 wt% to about 99 wt%. based on total weight of the catalyst.

[00017] In some embodiments, the catalyst may include zirconium in an amount of about 0.5% to about 70%, based on total weight of the catalyst. In some embodiments, the catalyst may include zirconium oxide in an amount of about 1 wt% to about 99 wt%, based on total weight of the catalyst.

[00018] In some embodiments, the yttrium-containing precursor may include yttrium nitrate, yttrium chloride, yttrium acetate, yttrium oxalate, yttrium hydroxide, yttrium organophosphate, yttrium alkoxide, yttrium carbonate, yttrium hydroxycarbonate, yttrium carboxylate, yttrium acetylacetonate, yttrium, yttrium oxide, or a combination thereof.

[00019] In some embodiments, the zirconium-containing precursor may include zirconium oxide, zirconium oxynitrate, zirconium chloride, zirconium acetate, zirconium oxalate, zirconium hydroxide, zirconium organophosphate, zirconium alkoxide, zirconium carbonate, zirconium hydroxycarbonate, zirconium carboxylate, zirconium acetylacetonate, zirconium, zirconium hydroxide, or a combination thereof.

[00020] In some embodiments, the yttrium-containing precursor, the zirconium-containing precursor or combination thereof is mixed with water or alcohol.

[00021] In some embodiments, the molar ratio of yttrium to zirconium is about 0.02 to about 50. In some embodiments, the catalyst may have a BET surface area of about 20 m^2/g to about 250 m^2/g. [00022] In some embodiments, the catalyst is a metal oxide catalyst.

[00023] In some embodiments, wherein the metal oxide catalyst has a surface with an M-0 site of the Lewis type and of balanced acid-base strength, wherein M comprises yttrium or zirconium..

[00024] In some embodiments, the method may further include cleaning a surface of the catalyst with a surface cleaning reagent. In some embodiments, the surface cleaning reagent may include dimethyl ether, ethylene, propylene, methanol, tert-butyl alcohol, methyl tertbutyl ether, di-tert-butyl ether, anisole, dimethyl carbonate, or combinations thereof. In some embodiments, the surface cleaning reagent may include dimethyl ether.

[00025] In some embodiments, the cleaning of the surface may remove excess water or CO2 through the surface cleaning reagent reacting with the water or CO2 species bound at the oxide surface.

[00026] In some embodiments, the method may further include cleaning a surface of the catalyst by heating the catalyst at a temperature of about 300°C to about 800°C. In some embodiments, wherein the cleaning does not include applying a surface cleaning reagent. In some embodiments, the cleaning may further include applying a surface cleaning reagent.

[00027] In another embodiment, a catalyst composition is provided. The catalyst composition may include the metal oxide/mixed metal oxide catalyst as prepared according to the method described herein.

[00028] In another embodiment, a method of performing a reaction using a catalyst composition is provided. The reaction may include alkane dehydrogenation, alkene hydrogenation, alkene dehydrogenation, olefin-paraffin alkylation, from CO/H2 mixtures without O-rej ection as H2O or CO2, C-C bond formation via alkene oligomerization or metathesis, dehydrocyclization (alkanes/alkenes to arenes), dehydrocyclodimerization (alkanes/alkenes to arenes with a larger number of C-atoms), transfer hydrogenation, hydroformylation/carbonylation, aromatization, dearomatization, reforming, isomerization, and bifunctional reactions in which one of the aforementioned functions can be combined with a Bronsted acid function. In some embodiments, the reaction may include alkane dehydrogenation. BRIEF DESCRIPTION OF THE DRAWINGS

[00029] FIG. 1 illustrates XRD-pattems of Zr-doped Y2O3 materials and reference Y2O3.

[00030] FIG. 2 illustrates XRD-pattems Y-doped ZrO2 materials and reference c-ZrO2 (cubic zirconia).

[00031] FIG. 3 illustrates a schematic experimental protocol employed for catalytic evaluation of Y2O3-ZrO2 catalysts.

[00032] FIG. 4 illustrates gravimetric rates of propane dehydrogenation at 723 K versus time on stream on different Y2O3-ZrO2 catalysts after pretreatment in He at 723K including a dashed line indicating homogeneous gas-phase reaction rate.

[00033] FIG. 5 illustrates gravimetric rates of propane dehydrogenation at 873 K versus time on stream on different Y2O3-ZrO2 catalysts after pretreatment in He at 873K; slope indicates deactivation rate constant.

[00034] FIG. 6 illustrates gravimetric rates of propane dehydrogenation at 723 K versus time on stream on different Y2Ch-ZrO2 catalysts after pretreatment in DME at 723 K.

[00035] FIG. 7 illustrates rates of propane dehydrogenation at 723 K versus time on stream on different Y2O3-Z1O2 catalyst with Y :Zr=20: 1 after various pretreatments.

[00036] FIGs. 8a-d are microscopic images showing the crystallini ty of a catalyst according to the present disclosure having a Y :Zr of 1 :4.

[00037] FIGs. 9a-b illustrate the distribution of Y and Zr throughout the cataly st of FIGs. 8a-d.

[00038] FIGs. lOa-d are microscopic images showing the crystallinity of a catalyst according to the present disclosure having a Y:Zr of 1 : 1.

[00039] FIGs. lla-b illustrate the distribution of Y and Zr throughout the catalyst of FIGs. lOa-d.

[00040] FIGs. 12a-d are microscopic images showing the crystallinity of a catalyst according to the present disclosure having a Y:Zr of 4: 1.

[00041] FIGs. 13a-b illustrate the distribution of Y and Zr throughout the catalyst of FIGs. 12a-d.

Definitions:

[00042] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[00043] As used herein, “a” or “an” entity refers to one or more of that entity, e.g., “a compound” refers to one or more compounds or at least one compound unless stated otherwise. As such, the terms “a” (or “an”), “one or more”, and “at least one” are used interchangeably herein.

[00044] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items. Additionally, as used herein, “or” means “and/or.”

[00045] The term “alkyl,” as used herein, refers to a saturated straight-chain (i.e., linear or unbranched) or branched hydrocarbon chain containing carbon atoms (such as. e.g., 1. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbon atoms). Unless otherwise specified, alkyl groups contain 1-20 carbon atoms. In some embodiments, alkyl groups contain 1-10 carbon atoms (denoted as Ci-io alky l herein). In some embodiments, alky l groups contain

1-8 carbon atoms (denoted as Ci-8 alkyl herein). In some embodiments, alkyl groups contain

1-6 carbon atoms (denoted as Ci-6 alkyl herein). In some embodiments, alkyl groups contain

1-4 carbon atoms (denoted as Ci-4 alkyl herein). In some embodiments, alkyl groups contain

1-3 carbon atoms (denoted as C1-3 alkyl herein). Nonlimiting examples of “alkyl” groups include methyl, ethyl, propyl, isopropyl, isobutyl, tert-butyl, sec-butyl, and the like.

[00046] The term “alkenyl,” as used herein, means a straight-chain (i.e., linear or unbranched) or branched hydrocarbon chain that contains at least one carbon-carbon double bond. Unless otherwise specified, alkenyl groups contain 2-20 (such as, e.g., 2-12, 2-6, or 2-4) carbon atoms. Nonlimiting examples of “alkenyl” groups include vinyl, allyl, butenyl, pentenyl, hexenyl, butadienyl. pentadienyl, hexadienyl, 2-ethylhexenyl, cyclopent-l-en-l-yl, and the like.

[00047] The term “alkynyl,” as used herein, means a straight-chain (i.e., linear or unbranched) or branched hydrocarbon chain that contains at least one carbon-carbon triple bond. Unless otherwise specified, alkynyl groups contain 2-20 (such as. e.g., 2-12, 2-6, or 2-4) carbon atoms. Nonlimiting examples of “alkynyl” groups include ethynyl. propynyl, butynyl. pentynyl, hexynyl, and the like.

[00048] The term “aryl” refers to monocyclic, bicyclic, and tricyclic ring systems having a total of five to fourteen ring members, wherein at least one ring in the system is aromatic and wherein each ring in the system contains 3 to 7 ring members. The term “aryl,” as used herein, also refers to heteroaryl ring systems as defined herein below. [00049] As used herein, the term “catalyst composition” refers to a composition comprising a material that promotes a chemical reaction.

[00050] As used herein, the term “increase” refers to altering positively, including, but not limited to, altering positively by 1%, altering positively by 5%, altering positively by 10%, altering positively by 25%, altering positively by 30% altering positively by 50%, altering positively by 75%, altering positively by 100%, altering positively by 200%, and the like.

[00051] As used herein, the term “decrease” refers to altering negatively, including, but not limited to, altering negatively by 1%, altering negatively by 5%, altering negatively by 10%, altering negatively by 25%, altering negatively by 30%, altering negatively by 50%, altering negatively by 75%, or altering negatively by 100%.

[00052] As used herein, the term “cleaning” refers to any process in which a catalyst is contacted with a chemical, combination of chemicals, or a series of chemicals to activate or reactivate the catalyst to a higher activity and/or selectivity state, either before using the catalyst for the intended chemical process or at intervening points in time during use of the catalyst.

[00053] As used herein, the term “impurity free” or “substantially free” refers to stream that comprises less than about 1 wt%, less than about 0.5 wt%, less than about 0.25 wt%, less than about 0. 1 wt%, less than about 0.05 wt%, less than about 0.01 wt%, or 0 wt% of a component, such as an impurity.

[00054] As used herein, the term “organic molecule” refers to molecules that are made of carbon and hydrogen, and can include other elements. Organic molecules must contain carbon atoms covalently bonded to hydrogen atoms (C-H bonds). They usually involve oxygen and can also contain nitrogen, sulfur, phosphorous, and others. Hydrocarbons, like alkanes, alkenes and alkynes are all organic molecules and so are alcohols, carboxylic acids and carbohydrates. Many organic compounds are formed from chains of covalently-linked carbon atoms with hydrogen atoms attached to the chain (known as a hydrocarbon backbone). This term involves, macromolecules, i.e. polymers.

[00055] As used herein, the term “surfactant” refers to a substance which tends to reduce the surface energy of a substrate when adsorbed to prevent particle agglomeration.

DETAILED DESCRIPTION OF THE PRESENT DISCLOSURE

[00056] The present disclosure relates to a process for preparing a metal oxide and/or mixed metal oxide catalyst that include Lewis Acid Base pairs (“LAB pairs”) that are active in hydrogenation and dehydrogenation reactions. The metal oxide and mixed metal oxide catalyst of the present disclosure include yttrium, zirconium, or a combination thereof. In some embodiments, the metal oxide or mixed metal oxide may include yttrium oxide, also known as yttria, zirconium oxide, also known as zirconia, or a combination thereof. Presently, metal oxide or mixed metal oxide catalysts including yttrium, zirconium or a combination thereof are being developed to enhance catalytic activity and/or thermal stability. These catalysts were found to have LAB pairs that are active during hydrogenation and dehydrogenation reactions. Without wishing to be bound by theory, it is surmised that exposing and having more active LAB pair sites increases the catalytic efficiency of the metal oxide and/or mixed metal oxide catalyst containing yttrium, zirconium, or a combination thereof. Thus, such catalyst has improved reactivity, selectivity and/or lifetime. To improve activation and/or reactivity of the catalyst, a method for preparing the catalyst is described herein.

[00057] By using the method as described herein, the inventors have surprisingly found that the resulting catalyst exhibited higher activity and stability at elevated temperatures when compared to reference materials synthesized using different methods and presented in the literature. Thus, the catalysts as prepared according to the method of the present disclosure can be utilized in a variety of reactions that involve LAB pairs, with a particular advantage in reactions where the stability of transition states is enhanced by interactions at LAB site pairs, leading to lower activation barriers.

[00058] The present inventors have found that LAB pairs that are typically blocked by water, carbon dioxide, and other titrant species including heteroatoms can act as highly active sites in catalyzing the dehydrogenation of alkanes. The sites that are most effective at stabilizing intermediates and transition states along a reaction sequence may also be those that strongly bind with reactants and/or titrants. However, the site accessibility requires that the surfaces are made and kept free of these bound molecules, such as water, carbon dioxide, or titrant species, which are commonly present during synthesis, thermal treatment, and/or exposure to ambient air. Trace impurities, such as oxygen, water, carbon dioxide, other titrant species during reaction, or precursors which can form titrants, may also be present in the reactant streams, which can affect the accessibility of the active sites. Thus, the activity and stability of the materials have been found to be linked to the ability of the system to keep inorganic surfaces (i.e., metal oxide surfaces) free of the basic molecules and their precursors. The method of the present disclosure helps to achieve freeing the active sites of a metal oxide and/or a mixed metal oxide catalyst including yttrium and/or zirconium, and thus making accessible the benefits of high cataly st surface area.

[00059] Thus, the present disclosure relates to a method of preparing a metal oxide and/or mixed metal oxide catalyst including yttrium, zirconium, or a combination thereof, having a BET surface area of about 20 m^2/g to about 250 m^2/g. For ease of describing the present disclosure, the catalyst will refer to a metal oxide and/or mixed metal oxide catalyst, unless stated otherwise. In some embodiments, the BET surface area may be about 20 m^2/g, about 30 m^2/g, about 40 m^2/g, about 50 m^2/g, about 60 m^2/g, about 70 m^2/g, about 80 m^2/g, about 90 m^2/g, about 100 m^2/g, about 110 m^2/g, about 120 m^2/g, about 130 m^2/g, about 140 m^2/g, about 150 m^2/g, about 160 m^2/g, about 170 m^2/g, about 180 m^2/g, about 190 m^2/g. about 200 m^2/g, about 210 m^2/g, about 220 m^2/g. about 230 m^2/g, about 240 m^2/g. or about 250 m^2/g. In some embodiments, the BET surface area may be about 20 m^2/g to about 300 m^2/g, about 20 m^2/g to about 250 m^2/g, about 50 m^2/g to about 160 m^2/g, about 50 m^2/g to about 130 m^2/g, or about 20 m^2/g to about 190 m^2/g.

[00060] In some embodiments, the catalyst may include yttrium. In other embodiments, the catalyst may include zirconium. In yet other embodiments, the catalyst may include yttrium and zirconium. In embodiments including both yttrium and zirconium in the metal oxide/mixed metal oxide catalyst, the molar ratio of yttrium to zirconium may be about 1 : 50 to about 50: 1 in the catalyst. In some embodiments, the molar ratio may be about 1 :50 to about 50: 1. about 1 :45 to about 45: 1, about 1

:40 to about 40: 1, about 1 :35 to about 35: 1. about 1 :30 to about 30: 1, about 1:20 to about 20: 1, about 1: 15 to about 5: 15, about 1 : 10 to about 10: 1, about 1:8 to about 8:1, about 1:5 to about 5:1, about 1:2 to about 2: 1 or about 1: 1.

[00061] In an embodiment, a method of preparing a metal oxide and/or mixed metal oxide catalyst including yttrium, zirconium, or a combination thereof is provided. The method includes mixing a zirconium-containing precursor, an yttrium-containing precursor or a combination thereof with a precipitant to obtain a mixture. The method further includes heating the mixture, and adding a surfactant comprising an organic molecule to the mixture. The method then further includes separating solids from the mixture, wherein the solids are the catalyst.

[00062] In some embodiments, the zirconium-containing precursor, if included, may be included in an amount of about 0.05 mol/L to about 1 mol/L, about 0.1 mol/L to about 0.95 mol/L, about 0.2 mol/L to about 0.8 mol/L, about 0.3 mol/L to about 0.7 mol/L. or about 0.4 mol/L to about 0.6 mol/L. In some embodiments, the zirconium-containing precursor, if included, may be about 0.05 mol/L, about 0.1 mol/L, about 0.143 mol/L, about 0.2 mol/L, about 0.33 mol/L, about 0.5 mol/L, about 0.8 mol/L, about 0.857 mol/L, about 0.9 mol/L, about 0.95 mol/L or about 1 mol/L.

[00063] In some embodiments, the zirconium-containing precursor may be zirconium oxide, zirconium oxynitrate, zirconium chloride, zirconium oxychloride, zirconium acetate, zirconium oxalate, zirconium organophosphate, zirconium alkoxide, zirconium carbonate, zirconium hydroxycarbonate, zirconium carboxylate, zirconium acetylacetonate, zirconium, zirconium hydroxide, or a combination thereof.

[00064] In some embodiments, the yttrium-containing precursor, if included, may be included in an amount of about 0.05 mol/L to about 1 mol/L, about 0.1 mol/L to about 0.95 mol/L, about 0.2 mol/L to about 0.8 mol/L, about 0.3 mol/L to about 0.7 mol/L. or about 0.4 mol/L to about 0.6 mol/L. In some embodiments, the yttrium-containing precursor, if included, may be included in an amount of about 0.05 mol/L, about 0.1 mol/L, about 0.143 mol/L, about 0.2 mol/L, about 0.5 mol/L, about 0.67 mol/L, about 0.8 mol/L, about 0.857 mol/L, about 0.9 mol/L, about 0.95 mol/L or about 1 mol/L.

[00065] In some embodiments, the yttrium-containing precursor may be yttrium nitrate, yttrium chloride, yttrium acetate, yttrium oxalate, yttrium hydroxide, yttrium organophosphate, yttrium alkoxide, yttrium carbonates, yttrium hydroxy carbonate, yttrium carboxylate, yttrium acety lacetonate, yttrium, yttrium oxide, or a combination thereof.

[00066] In some embodiments, the precipitant may include a basic compound. In some embodiments, the basic compound may include Bronsted bases and Lewis bases. For example, the basic compound may be an alkali metal hydroxide, alkaline earth metal hydroxide, ammonia, alkylammonium hydroxides, or a combination thereof. In some embodiments, the basic compound may be sodium hydroxide, potassium hydroxide, barium hydroxide, ammonia, or a combination thereof.

[00067] In some embodiments, the mixing is performed to form a homogenized mixture of components. The mixing may be formed by stirring, swaying, shaking, rolling, rotating and/or Bonification, while the precursors and precipitant are in a solvent. Thus, the mixture formed with the precursors and precipitant form a suspension that is further treated so that solids are separated out.

[00068] In some embodiments, the heating of the mixture may be carried out at a temperature in a range from about 50°C to about 250°C. In some embodiments, the heating may be at a temperature of about 50°C. about 60°C, about 70°C, about 80°C, about 90°C, about 100°C. about 110°C, about 120°C. about 130°C, about 140°C. about 150°C, about 160°C. about 170°C, about 180°C, about 190°C, about 200°C, about 210°C, about 220°C, about 230°C, about 240°C, or about 250°C. In some embodiments, the heating may be at a temperature of about 50°C to about 250°C, about 50°C to about 200°C, about 80°C to about 200°C, or about 80°C to about 180°C. In some embodiments, the heating of the mixture may be carried out for about 1 hour to about 24 hours. In some embodiments, the heating may be carried out for about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, about 12 hours, about 13 hours, about 14 hours, about 15 hours, about 16 hours, about 17 hours, about 18 hours, about 19 hours, about 20 hours, about 21 hours, about 22 hours, about 23 hours, or about 24 hours.

[00069] In some embodiments of the method, the surfactant including an organic molecule may include a carboxylic acid, a carboxylate anion, a carboxylic salt, or a combination thereof. In some embodiments, the carboxylic acid may include lauric acid, or its laureate form. The organic molecule is believed to stabilize the mixture during the method of preparing so that solids may form.

[00070] In some embodiments, separating of the solids from the mixture may include filtering the solids, decanting the solids, or centrifuging the mixture, or any other method known to one of skill in the art.

[00071] In some embodiments, the method may further include washing the solids with a hydroxide, alcohol, water, or a combination thereof. The hydroxide may include ammonium hydroxide, sodium hydroxide, or a combination thereof. In an embodiment, the hydroxide is ammonium hydroxide. In another embodiment, the hydroxide is a sodium hydroxide. In some embodiments, the hydroxide may be a solution having a pH of about 7 to 10, or about 9.

[00072] In some embodiments, the method may further include drying the solids. In some embodiments, the drying may be carried out at a temperature of about 25°C to about 110°C. In some embodiments, the drying may be at a temperature of about 25°C, about 35°C, about 45°C, about 55°C, about 65°C, about 75°C, about 85°C, about 95°C, about 100°C, or about 110°C.

[00073] In some embodiments, the method may further include calcining the solids. In some embodiments, the calcining may be carried out at a temperature of about 300°C to about 800°C. In some embodiments, the calcining may be at a temperature of about 300°C, about 325°C, about 350°C, about 375°C, about 400°C, about 425°C, about 450°C, about 475°C, about 500°C, about 525°C, about 550°C, about 575°C, about 600°C, about 625°C, about 650°C, about 675°C. about 700°C. about 725°C. about 750°C. about 775°C, or about 800°C. In some embodiments, the calcining may be carried out for about 2 hours to about 12 hours. In other embodiments, the calcining may be carried out for about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 11 hours, or about 12 hours. [00074] In some embodiments, the catalyst prepared according to the method herein may include yttrium in an amount of about 0.3% to about 80%, based on total weight of the catalyst. In some embodiments, the catalyst includes yttrium in an amount of about 0.3%, about 0.5%, about 1%, about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 65%, about 70%, about 75%, or about 80%, based on total weight of the catalyst.

[00075] In some embodiments, the catalyst prepared according to the method herein may include yttrium oxide in an amount of about 1 wt% to about 99 wt%, based on total weight of the catalyst. In some embodiments, the catalyst includes yttrium oxide may include about 1 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%. about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, about 80 wt%, about 85 wt%, about 90 wt%, about 92 wt%, about 95 wt%, or about 99 wt%, based on total weight of the catalyst.

[00076] In some embodiments, the catalyst prepared according to the method herein may include zirconium in an amount of about 0.5% to about 70%, based on total weight of the catalyst. In some embodiments, the catalyst may include zirconium in an amount of about 0.5%, about 1%, about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 65%, or about 70%, based on total weight of the catalyst.

[00077] In some embodiments, the catalyst may include zirconium oxide in an amount of about 1 wt% to about 99 wt%, based on total weight of the catalyst. In some embodiments, the catalyst includes zirconium oxide may include about 1 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%,

about 35 wt%, about 40 wt%, about 45 wt%, about 50 wt%, about 55 wt%, about 60 wt%, about 65 wt%, about 70 wt%, about 75 wt%, about 80 wt%, about 85 wt%, about 90 wt%, about 92 wt%, about 95 wt%, or about 99 wt%, based on total weight of the catalyst.

[00078] In some embodiments of the method, the yttrium containing precursor, zirconium containing precursor or a combination thereof may be mixed with water. In some embodiments, the yttrium containing precursor, zirconium containing precursor or combination thereof may be mixed with a solvent. The solvent may include an alcohol, water or a combination thereof. The alcohol may be methanol, ethanol, w-propanol, or isopropanol.

[00079] In some embodiments, the catalyst prepared by the method of the present disclosure may include yttrium and zirconium, wherein the molar ratio of yttrium to zirconium is about 0.02 to about 50, about 0.05 to about 20, about 0.1 to about 15, about 5 to about 12, or about 8 to about 10. In some embodiments, the molar ratio of yttrium to zirconium may be about 0.02, about 0.05. about 0.1, about 0.5. about 1, about 3. about 5, about 8, about 10, about 12, about 15, about 18, about 20, about 25, about 30, about 35, about 40, about 45, or about 50.

[00080] In some embodiments, the catalyst may be a metal oxide catalyst including yttrium, or zirconium, or a combination thereof as the metal. The metal oxide catalyst as described herein may have a surface with an M-0 site of the Lewis type and of balanced acid-base strength, wherein M includes yttrium or zirconium. In some embodiments, the catalyst may be a mixed metal oxide catalyst including yttrium and zirconium as the metal. The mixed metal oxide catalyst may have a surface with an M-0 site of the Lewis type and of balanced acidbase strength, wherein M includes yttrium and zirconium.

[00081] In some embodiments, the method may further include mixing an additional precursor. The additional precursor may include a rare earth oxide or a rare earth metal. If included, the additional precursor may be included in an amount of 5 wt% or less, based on total weight of the catalyst.

[00082] In some embodiments, the additional precursor may include alumina. In some embodiments, alumina may be aluminum salts, aluminum oxide hydroxides, aluminum hydroxides, alumina, or a combination thereof. In some embodiments, the alumina may be aluminum sulfates, aluminum nitrates, aluminum phosphates, aluminum chlorides, aluminum bromides, aluminum acetates, diaspore, boehmite, akdalaite, gibbsite, bayerite, doyleite, nordstrandite, or a combination thereof. In some embodiments, the alumina may include colloidal alumina, colloidal alumina oxide hydroxides, colloidal aluminum hydroxides, or a combination thereof.

[00083] In some embodiments, the method of the present disclosure may further include cleaning a surface of the catalyst with a surface cleaning reagent. In some embodiments, the surface cleaning reagent may include dimethyl ether, ethylene, propylene, or other alkenes or cycloalkenes as suitable, methanol, tert-butyl alcohol, methyl-tert-butyl ether, di-terf-butyl ether, anisole, dimethyl carbonate, or a combination thereof. In some embodiments, the surface cleaning reagent may include dimethyl ether. In some embodiments, the surface cleaning reagent may include an olefin, such as a C2-C4 olefin.

[00084] In some embodiments, the method may further include cleaning a surface of the catalyst from carbonaceous deposits by heating the catalyst at a temperature of about 300°C to about 800°C in the presence of O2, followed by an inert purge period of about 5 minutes to about 60 minutes to remove residual O2. In some embodiments, the heating may be at a temperature of about 300°C, about 350°C, about 400°C, about 450°C, about 500°C, about 550°C, about 600°C, about 650°C, about 700°C, about 750°C, or about 800°C. In some embodiments, the inert purge period may be about 5 minutes, about 10 minutes, about 15 minutes, about 20 minutes, about 25 minutes, about 30 minutes, about 35 minutes, about 40 minutes, about 45 minutes, about 50 minutes, about 55 minutes, or about 60 minutes.

[00085] In some embodiments, the cleaning of the surface removes excess water through the surface cleaning reagent reacting with the water or carbon dioxide species bound at the oxide surface.

[00086] In some embodiments, the method may further include cleaning a surface of the catalyst by heating the catalyst at a temperature of about 300°C to about 800°C. In some embodiments, the heating may be at a temperature of about 300°C, about 350°C, about 400°C, about 450°C, about 500°C. about 550°C, about 600°C, about 650°C, about 700°C, about 750°C, or about 800°C.

[00087] In some embodiments, when the cleaning includes heating the catalyst, it does not include applying a surface cleaning reagent. In other embodiments, when the cleaning includes heating the catalyst, it may further include applying a surface cleaning reagent.

[00088] In some embodiments, a catalyst composition may include the catalyst prepared according to the method described herein. The catalyst composition may include a catalyst, catalyst support, a catalyst binder and/or a catalyst component used in a catalyst for the dehydrogenation of hydrocarbons.

[00089] In some embodiments, a method of performing a reaction using a catalyst composition is provided. The reaction may include alkane dehydrogenation, alkene hydrogenation, alkene dehydrogenation, olefin-paraffin alkylation, from CO/H2 mixtures without O-rej ection as H2O or CO2, C-C bond formation via alkene oligomerization or metathesis, dehydrocyclization (alkanes/alkenes to arenes), dehydrocyclodimerization (alkanes/alkenes to arenes with a larger number of C-atoms), transfer hydrogenation, hydroformylation/carbonylation, aromatization, dearomatization, reforming, isomerization, and bifunctional reactions in which one of the aforementioned functions can be combined with a Bronsted acid function. In some embodiments, the reaction may include alkane dehydrogenation. In some embodiments, the reaction may include the dehydrogenation of propane or other alkanes, as well as other related C-H and H-H cleavage formation reactions.

[00090] In some embodiments, the method may further include pretreating the catalyst composition in an aerobic oxidative environment before or after the cleaning with the surface cleaning reagent and treating the reactants with a trap. [00091] In some embodiments, the method may further include pretreating the catalyst composition in an aerobic oxidative environment before the cleaning with the surface cleaning reagent and treating the reactants with a trap.

[00092] In some embodiments, the method may further include pretreating the catalyst composition in an aerobic oxidative environment after the cleaning with the surface cleaning reagent and treating the reactants with a trap to prevent titrants from re-entering the stream and blocking the most competent LAB pairs.

[00093] Claims or descriptions that include “or” or “and/or” between at least one members of a group are considered satisfied if one, more than one, or all of the group members are present in, employed in, or otherwise relevant to a given product or process unless indicated to the contrary or otherwise evident from the context. The disclosure includes embodiments in which exactly one member of the group is present in, employed in, or otherwise relevant to a given product or process. The disclosure includes embodiments in which more than one, or all the group members, are present in, employed in, or otherwise relevant to a given product or process.

[00094] Furthermore, the disclosure encompasses all variations, combinations, and permutations in which at least one limitation, element, clause, and descriptive term from at least one of the listed claims is introduced into another claim. For example, any claim that is dependent on another claim can be modified to include at least one limitation found in any other claim that is dependent on the same base claim. Where elements are presented as lists, such as, e g., in Markush group format, each subgroup of the elements is also disclosed, and any element(s) can be removed from the group. It should be understood that, in general, where the disclosure, or aspects of the disclosure, is/are referred to as comprising particular elements and/or features, embodiments of the disclosure or aspects of the disclosure consist, or consist essentially of, such elements and/or features. For purposes of simplicity, those embodiments have not been specifically set forth in haec verba herein. Where ranges are given (such as, e.g., from [X] to [Y]), endpoints (such as, e g., [X] and [Y] in the phrase “from [X] to [Y]”) are included unless otherwise indicated. Furthermore, unless otherwise indicated or otherwise evident from the context and understanding of one of ordinary skill in the art. values that are expressed as ranges can assume any specific value or sub-range within the stated ranges in different embodiments of the disclosure, to the tenth of the unit of the lower limit of the range, unless the context clearly dictates otherwise. [00095] Those of ordinary skill in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the disclosure described herein. Such equivalents are intended to be encompassed by the following claims.

EXAMPLES

[00096] The following examples are intended to be illustrative and are not meant in any way to limit the scope of the disclosure.

[00097] Several tests were conducted to test various materials for dehydrogenation reactions that could benefit from thermal or chemical treatments and may remove impurities from the stream and from the surface of the catalysts. Tests were also conducted to measure the reaction rates as one of the means to assess the benefits of such treatments.

1. Preparation of Yttria-doped Zirconia and Zirconia-doped Yttria

[00098] Yttria-doped zirconia mixtures and vice versa were prepared using a hydrothermal synthesis method adapted from WO 2016/071449A1. Typically. 200 mL of a 1 molar metal solution of ZrO(NOs)2 XH2O and/ or in combination with YtNO.fia 6H2O, where the sum of concentrations of ytrrium and zirconium give 1 mol/L, e.g., 0.05 mol/L Y(NOs)3 6H2O and 0.95 mol/L ZrO(NOs)2 XH2O, in deionized water were prepared in a beaker and stirred until a homogeneously clear solution was obtained (variations range from pure ZrCh, Y-doped ZrCh, Zr-doped Y2O3 and pure Y2O3). A solution of ammonium hydroxide (25%) was used to induce co-precipitation of the used metal precursors at a constant pH level of 9. Therefore, in a precipitation vessel (2 L size), 200 mL of deionized water were dosed prior to the precipitation to adjust the filling level of the vessel and then, the pH level was set to 9 prior to dosage of the metal containing solution. The metal precursor solution was then continuously dosed over the course of 15 minutes, while ammonium hydroxide was dosed in the same manner to ensure a constant pH level during the whole procedure. After the complete dosage, the formed suspension was stirred for additional 15 minutes at room temperature in the vessel before the suspension was filtered using a Btichner-funnel with a blue ribbon filter. The wet filter cake was transferred into a Teflon lined stainless steel autoclave with a maximum fill quantity of 50% and aged at 423 K for 2 h. The aged material was allowed to cool down to room temperature overnight. Afterw ards, the material w as transferred into a beaker and 0.22 mol of lauric acid (according to 22% of total molar metal ratio) were added to the mixture and subsequently diluted in 200 mL of deionized water. The suspension was stirred for at least 3 hours at room temperature. Following, the mixture was filtered using a Buchner-funnel with a blue ribbon filter. The formed filter cake was washed with ammonium hydroxide solution until the filtrate was nitrate free. Then, the filter cake was dried at 313 K for 16 hours and subsequently calcined at 873 K for 4 hours with a ramp rate of 4K/min.

[00099] In total, 12 Examples were prepared with this method, comprising the pure metal oxides as well as distinct Y:Zr-ratios, denoted as Example- 1 to Example-12.

X-Ray Diffraction Analysis

[000100] For structural characterization, the prepared materials were analyzed using a Bruker D8 Advance A25-XI-IA22C4B-diffractometer system with a 3 kW generator (Cu-source, 20 - 50 kV / 5 - 60 mA) in Bragg-Brentano geometry. A Lynxeye XE detector (1 -dimensional / compound silicon strip/ high resolution) was used to collect the signals. The diffraction patterns were measured from 10 - 90 20 with a scan rate of 0.02 2 0 /s. Interpretation was done using reference patterns of the respective phases according to the inorganic crystal structure database (ICSD).

X-Ray Fluorescence Analysis

[000101] The elemental composition was measured using a Bruker Nano M4 Tornado micro XRF-spectrometer with motorized X-Y stage equipped with a Rhodium-Silicon-Drift-Detector with a maximum voltage of 50 kV and 600 pA current. The spot size of the materials was below 20 pm and for each sample 20 spots were measured with a recording time of 60 s per spot.

Simultaneous Thermo gravimetric Analysis

[000102] The prepared materials were analyzed for mass change and thermal load upon their calcination temperature using a Netzsch STA 449 F3 Jupiter thermoanalyzer. Measurements were ranging from 298 K (about 25°C) until 1273 K with a heating ramp of 10 K/min in an atmosphere consisting of clean dry' air with a flow of 50 mL/min.

Nitrogen Physisorption Measurements

[000103] Surface area measurements according to BET-theory were conducted with a Micrometrics TriStar II 3020 physisorption device. Pre-conditioning of samples including degassing was done at 423 K (about 150°C) in vacuo for 2 hours. Physisorption was recorded at the boiling temperature of liquid nitrogen (77 K) in the pressure range P/Po of 0.002 - 0.20. [000104] Table 1 shows the experimentally measured percentage of metal contents (excluding O) of the prepared materials. It is noted that Hafnium (Hf) is a common impurity in Zr-containing precursors, but exhibits comparable chemical properties to Zr. The metal contents were normalized to 100%. The obtained metal contents are in good agreement with the target stoichiometries.

Table 1. Obtained metal contents and corresponding Y :Zr ratio.

[000105] The corresponding surface areas according to BET-analysis, crystallite sizes as well as lattice parameters after Rietveld refinement are presented in Table 2. The surface area of Y-doped ZrO2 increases with higher Y-contents, showing a constructive synergy between the formed Y2O3 and ZrO2 species. The same is observable for the Zr-doped Y2O3. Note, that during Rietveld refinement, the cubic phase of ZrO2 was used. It is observable, that with increasing Y -content in Y -doped ZrO2, the lattice parameter increases while the crystallite size decreases, highlighting a higher ordered structure with lower Y-contents. Vice versa, increasing the Zr-content in Zr-doped Yttria, the lattice parameter lowers in correlation with an increase in crystallite size, assuming that a conglomerate of Y2O3 and ZrCh particles have formed. This observation is evident with Examples 10 to 12, where secondary' phases of ZrCh or a ZrCh-phase in a ratio of Y:Zr = 1 : 1 is found. Table 2. Surface area, crystallite size and lattice parameter of found phases for the prepared examples, corresponding to certain Y:Zr ratios.

[000106] Further, X-Ray diffractograms of selected Examples are shown in Figures 1-X. Figure 1 represents the Zr-doped Y2O3 materials. At a low Y:Zr ratio, the presence of a secondary ZrCh phase is observable. Figure 2 shows the Y-doped ZrCh samples. It was found that pure ZrCh leads to the formation of a monoclinic phase, while already low' level of Y- doping, the cubic phase has formed.

Comparative Example 1: Monoclinic-ZrCh (in- ZrOz)

[000107] Monoclinic-ZrCh (m-ZrCh) was prepared using hydrothermal synthesis methods using the decomposition of urea to gradually increase the solution pH and induce precipitation as described in Li. W. et al. "'Facile Synthesis of Pure Monoclinic and Tetragonal Zirconia Nanoparticles and Their Phase Effects on the Behavior of Supported Molybdena Catalysts for Methanol Selective Oxidation" Langmuir 2008, 8358-8366. ZrO(NO3)2 xH20 (12.7 g; Sigma- Aldrich) and CO(NH2)2 (21.6 g; Sigma-Aldrich) were each dissolved in deionized water (^ 17.6 M -cm resistivity; 30 g) at 323 K. The two solutions were mixed in a Teflon- lined autoclave (Parr, 125 cm3) and held at 393 K for 20 h. The powders formed were rinsed with deionized water (250 g) and centrifuged four times followed by treatment in ambient air at 393 K for 12 h. These samples were then treated in flowing He (Praxair. 99.999%, 1.6 cm3 g-1 s-1) at 723 K for 5 h.

2. Z1O2-Y2O3 catalysts for propane dehydrogenation reaction

[000108] A series of earth-abundant oxides composed of yttria and zirconia (ZrO2-Y2Os), see Examples 1-12 above, were evaluated as catalysts for propane non-oxidative dehydrogenation (PDH). Tests were carried out in a straight top-dow n plug-flow' quartz reactor (inner diameter 6 mm) using around 20 mg of material in the form of sieved aggregates (0. 18-0.36 mm). They were physically mixed with quartz powder to achieve catalyst dilution ratio (by mass) of 50 g quartz (g catalyst)$^{'1}$. The reactor was resistively -heated using an Applied Test Systems 3210 series furnace, temperature was controlled using a Watlow 96 controller connected to a K-type thermocouple contacting the depth of a dimple located on the w'all of the quartz reactor in the middle of the catalyst bed. Gases were introduced to the system using mass flow controllers. Reactant mixtures were additionally purified by flowing through O2/H2O scrubber (Agilent 5182-9401, 5 ppb) positioned directly prior to the reactor. Catalysts were tested using the protocol comprising 5 steps described below and summarized in Figure 3.

Pretreatment in He at 723K and PDH reaction at 723K

[000109] Catalyst was kept in flowing He (Praxair, 99.999%) at 50 cm^3 g$^{'1}$ s$^{'1}$ while increasing the temperature from ambient to 723 K at 0.33 K s$^{'1}$ and holding for 3.6 ks. Afterwards, the propane dehydrogenation reaction was carried out. For this, a flow of Cd Is (7.5 kPa), H2 (5 kPa), Ar (7.5 kPa) balanced with He (near ambient total pressure) was introduced at 50 cm^3 g$^{'1}$ s$^{'1}$ flow rate. The reaction was carried out for 4 ks. See Fig. 4.

Pretreatment in He at 873K and PDH reaction at 873K

[000110] After the PDH reaction at 723 K, gas flow was switched to He at 50 cm^3 g$^{'1}$ s$^{'1}$ while increasing the temperature from 723 to 873 K at 0.33 K s$^{'1}$ and holding for 1 h.

Afterwards, the propane dehydrogenation reaction was carried out at 873 K for about 8 ks using the gas flow of composition identical to the described above for the reaction at 723 K. See Fig. 5.

Temperature-programmed cooling from 873 K to 723 K

[000111] After 8 ks of reaction, the temperature was decreased from 873 K to 723 K at 0.067 K s$^{'1}$ while the PDH reaction continued. After the reaction, visual inspection showed that catalyst bed color was dark grey, potentially indicating coke formation.

Catalyst regeneration at 723K by oxygen treatment

[000112] After temperature stabilized at 723 K, catalyst was treated in He for 600 s and afterwards in Ch/He (5 kPa O2 balanced with He) for 1.2 ks followed by another treatment in He for 0.6 ks. Visual inspection showed any previously present dark catalyst bed colors were changed to white because of coke oxidation.

Pretreatment in dimethyl ether at 723 K and PDH reaction at 723K

[000113] After oxygen treatment, the catalyst was subjected to a surface chemical cleansing protocol by exposure to a chemical stream of 1.25 kPa dimethyl ether (Praxair, 5.07±0.2% DME, 5.07±0.2% Ar, balance He) at 50 cm^3 g$^{'1}$ s$^{'1}$ for 0.25 h at 723 K, followed by a He purge period of 0.42 h to remove residual DME and byproducts. Afterwards, the PDH reaction was carried out at 723 K. See Fig. 6.

Pretreatment in He at 723k and PDH reaction at 723K

[000114] Figure 4 shows gravimetric dehydrogenation rates for a series of ZrO2-Y2Os catalysts after a pretreatment in He at 723 K and subsequent PDH reaction at 723 K versus time on stream. The dashed lines in Figure 4 indicate rates observed in blank test where no catalyst has been loaded and corresponds to the superposition of gas-phase reaction and/or reactions on the wall or dilutant.

[000115] Catalyst composition impacts the transient reactivity of PDH reactions. For ZrCh and materials with Y:Zr ratio between 1:20 and 1:4 (Examples 1-6), the PDH rate increases with time on stream and reaches a steady-state level between 0.015 and 0.02 mol h$^{'1}$ kg$^{'1}$ kPa$^{" 1}$ after 2 ks. This is in line with previous results where an activation is related to the surface cleaning by propylene, formed as a product of PDH, under anhydrous conditions, which is formed during PDH reaction, and a steady state rate that corresponds equal rates of surface cleaning and site titration by impurities in the feed. Catalysts with higher yttrium contents (for Y:Zr ratio of 1:1 and above) do not show activation, instead, a slight deactivation followed by a steady state is observed. The gravimetric steady -state rate was about 0.01 mol h$^{'1}$- kg ^{1} kPa ^{1} for all the materials. A blank experiment was carried out where no catalyst has been loaded. The blank experiment was used to the estimate the contribution of gas-phase reaction and/or reactions on the wall or dilutant. The dehydrogenation rate of the blank (dashed line in Fig. 4) in this experiment corresponded to 0.007 mol h ^kg ^kPa ^{1} for virtual loading of 20 mg of catalyst, which is close to the steady-state reaction rates observed for yttria-rich catalysts. This indicates deactivation of the corresponding materials to almost complete deactivation, contrary to zirconia-rich materials demonstrating steady-state rates higher than observed in the blank experiment.

[000116] An increase in reaction temperature up to 873 K led to noticeable changes in catalytic behavior, as shown in Fig. 5. For catalysts with low yttrium content (Y:Zr ratio 1 :4 and below) the activation of sample was still observed and was more pronounced. After 2 ks time on stream dehydrogenation rates reach steady state levels. These rates are 2 orders of magnitude higher than observed at 723 K; between 2.5 and 4.3 mol h ^kg ^{1} kPa ^{1}. These rates are affected by catalyst composition, believed to be dictated by superposition of number of sites, their activity in PDH reaction and tendency to be titrated by impurities in the feed. Interestingly, for catalyst with higher yttrium content (Y:Zr ratio 1: 1 and above), a different evolution of dehydrogenation rates was observed. At first, rates increased, reaching a maximum and afterwards exponentially decreased. The deactivation constants increase with increase in yttrium content from 0. 19 ks^{-1} for the material with Y :Zr=l : 1 ratio to 0.49 ks$^{'1}$ for Y2O3. Such a behavior suggests that the deactivation is caused not by a titration of sites with water, but by a formation of carbonaceous deposits blocking the active sites, possibly due to less selective PDH which enables non-negligible C-C bond breaking reactions. Pretreatment in dimethyl ether at 723 K and PDPI reaction at 723K

[000117] The limited catalytic activity' at 723 K is known to be a consequence of surface coverage titrants, preferably water molecules. A way to enhance dehydrogenation rates is chemical cleaning of surface by reacting surface hydroxyl groups with cleaning agent, for example dimethy l ether.

[000118] Figure 6 shows the gravimetric rates of propane dehydrogenation at 723 K versus time on stream on different Y2O?-ZrO2 catalysts after pretreatment in DME at 723 K. For ZrCh sample rates decrease exponentially, as was previously reported. The deactivation constant for ZrCh sample (0.8 ks$^{'1}$) from Example 5 is significantly higher than that for m-ZrCh material synthesized in Comparative Example 1 (deactivation constant was 0.2 ks$^{'1}$). (See WO 2023/056231 and US 2023/0303465). This might be partially an effect of much lower surface area (BET surface area 38 m^2 g" for ZrO2 sample from Example 5 vs ~ 130 m^2 g" for m-ZrO2 sample synthesized at Comparative Example 1) and, consequently, lower number of active sites and/or stronger binding of titrant molecules.

[000119] For the materials with low yttrium content (Y :Zr ratio 1:4 and below. Examples 1- 5), there is an activation period, which w e associate with the formation of some “DME debris” which require higher temperature to be decomposed. For the materials with high yttrium content (Y:Zr ratio from 1: 1 to 1 :20), the initial rates were between 2.0 and 2.5 mol h" kg' ' kPa$^{'1}$, where rates at first decreased rapidly and afterwards decrease exponentially monotonically. The deactivation constants tend to

increase with increase in yttrium content from 0.3 ks'^{1} for Y:Zr=l : 1 to 0.41 for Y:Zr=20: l . For Y2O3 the initial rates are 0.9 mol h'^{1} kg' '•kPa'^{1} and exponentially decrease with deactivation constant being 0.43 ks'^{1}.

[000120] Interestingly, for catalysts with high yttrium content (Y:Zr ratio with Y content above 1 : 1). a second DME treatment does not fully restore the catalytic activity (as can be seen in Figure 7), yet the combination of oxygen treatment followed by DME treatment does restore to the initial activity. This indicates that at high yttrium content the deactivation is caused not only by titration of LAB with w ater, but also by formation of carbonaceous deposits, requiring oxygen treatment for the regeneration and causing deactivation at 873 K, as hypothesized above.

Crystallization study

[000121] Additional samples w ere prepared according to the method described herein with different ratios of Y to Zr. In Sample 1, a metal oxide catalyst having a ratio of Y:Zr of 1:4 was prepared. In Sample 2, a metal oxide catalyst having a ratio of Y:Zr of 1 : 1 was prepared. In Sample 3, a metal oxide catalyst having a ratio of Y:Zr of 4: 1 was prepared. For each sample, high angle annular dark-field transmission electron microscopic (HAADF-TEM) images were taken to show crystal morphology and energy’ dispersive X-Ray (EDX) composition analysis was performed to show the distribution of Y and Zr throughout the catalyst.

[000122] Figs. 8a to 8d show the HAADF-TEM images of Sample 1, while Figs. 9a and 9b show the EDX mapping of Y and Zr in the catalyst. Figs. 10a to lOd show the HAADF-TEM images of Sample 2, while Figs. l la and l ib show the EDX mapping of Y and Zr in the catalyst. Figs. 12a to 12d show the HAADF-TEM images of Sample 3, while Figs. 13a and 13b show the EDX mapping of Y and Zr in the catalyst.

[000123] As can be seen in Figs. 8a to 8d, 9a and 9b. Sample 1 consist of aggregated nanoparticles with size ~10 nm with homogeneous Y and Zr distribution. The images show a fine-crystalline phase that is similar to cubic Y-dopped ZrCh (cubic). Similarly, Figs. 12a to 12d, 13a and 13b of Sample 3 show that the nanoparticles are somewhat larger. In contrast, for Sample 2 two different crystal types were observed. Sample 2 had a fine-particulate phase made of aggregated nanoparticles, similar to Samples 1 and 3, and a crystalline phase made of needle-like particles. This second phase is similar to Y2O3 (cubic).

[000124] The concentration ratios of Samples 1 to 3 were also calculated and are shown in Table 3.

Table 3

[000125] It was also found that none of Samples 1 to 3 had Y enrichments at needle-like particles, consistent with previous suggestion that these crystals are Y2O3 phase.

[000126] The present invention has been described with reference to specific exemplary embodiments thereof. The specification and drawings are, accordingly, to be regarded in an illustrative rather than a restrictive sense. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art and are intended to fall within the scope of the appended claims.

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Publication number	Priority date	Publication date	Assignee	Title
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Title
LI. W. ET AL.: "Facile Synthesis of Pure Monoclinic and Tetragonal Zirconia Nanoparticles and Their Phase Effects on the Behavior of Supported Molybdena Catalysts for Methanol Selective Oxidation", LANGMUIR, 2008, pages 8358 - 8366

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Priority And Related Applications

Applications Claiming Priority (2)

Application	Filing date	Title
US202463635767P	2024-04-18	
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Legal Events

Date	Code	Title	Description
2025-12-03	121	Ep: the epo has been informed by wipo that ep was designated in this application	**Ref document number**: 25727569 **Country of ref document**: EP **Kind code of ref document**: A1

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