

A METHOD OF PREPARING A CATALYST AND A CATALYST PREPARED FROM THE METHOD

CROSS REFERENCE TO RELATED APPLICATION

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The present application claims priority to Singapore application number 10202011858S filed on 27 November 2020, the contents of which are incorporated by reference.

TECHNICAL FIELD

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The present invention relates generally to a method of preparing a catalyst and a catalyst prepared according to the method as described herein. The present invention also relates to a process of converting propane to propylene using the catalyst described herein.

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BACKGROUND ART

Olefins and its derivatives are counted amongst one of the most commercially important chemicals in the industry. The major production of propylene worldwide comes from steam cracking or catalytic cracking of naphtha; however, anthropological activities and the rate of technological progress have caused a steady decline in petroleum reserves, driving the need to look for alternative sources of propylene. To this end, propane dehydrogenation is considered as one of the most energy efficient and viable route for the selective production of propylene with significantly smaller fraction of hydrocarbon side-products. The benefit of lesser side-products makes the downstream separation process more economical as compared to the naphtha cracking process which yields significantly more unwanted side-products.

From the current state of the art in developing highly active, selective, and stable catalysts for propane dehydrogenation, synthesis of highly dispersed single-site catalysts has gained increasing attention. This can be attributed to the catalysts having a high catalytic surface area yet remaining resistant to sintering at high temperature and pre-treatment conditions. There is generally a treatment step involving the use of highly concentrated acid as a peptizing agent to form a viscous matter for extrusion of a catalyst. However, the use of highly concentrated acid remains unfavourable for scalability as additional safety and operation measures are necessary when handling large amounts of concentrated acid.

Various types of synthesis processes have been proposed for producing highly dispersed single-site catalysts, including organometallic precursor routes, sol-gel synthesis, atomic layer deposition and strong electrostatic adsorption steps. However, all these processes are largely complex and expensive, involving the utilization of complex chemicals during their synthesis and post-treatment steps. For example, many organometallic complexes are air or moisture sensitive and require the use of inert atmosphere conditions (e.g. Schlenk lines) for proper handling and usage. Further, the synthesis of organometallic complexes generally comprises the use of various precursors and multiple steps which makes it expensive and undesirable for scalability.

Therefore, there is a need to provide for a method of preparing a catalyst to address one or more of the problems discussed above.

SUMMARY

In one aspect, the present disclosure relates to a method of preparing a catalyst comprising the steps of:

- (a) adding a precursor of alumina, a precursor of heteroatom oxide, and one or more precursors of metals into a solution containing a surfactant to obtain a mixture;
- (b) filtering and/or drying the mixture of step a) to obtain a solid powder; and
- (c) calcining the solid powder obtained in step c) to afford a catalyst.

Advantageously, the method is facile, requiring fewer steps and time to prepare the catalyst. The method may optionally not require the use of highly concentrated acid, which is used in a conventional process, as mentioned above. As the disclosed method does not use highly concentrated acid, the disclosed method may be favourable for scalability.

Further advantageously, the method is a one-pot synthesis method to afford the highly dispersed sites of the catalyst, as compared to the complex organometallic route of synthesis mentioned above, which is not able to produce catalysts having highly dispersed active sites.

In another aspect, the present disclosure relates to a catalyst, comprising an alumina support with highly dispersed heteroatom oxide doping; and one or more metals highly dispersed within or thereon the alumina support.

Advantageously, the heteroatom may form a homogenous phase with the alumina support for higher dispersion and isolation of active sites, resulting in the catalyst achieving high surface area, high catalytic activity, high selectivity, and high stability.

The catalyst may be prepared according to the method as described herein.

In another aspect, the present disclosure relates to a process of converting propane to propylene comprising the step of heating a flow of propane in the presence of the catalyst as described herein.

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DEFINITIONS

The term “alkyl” as used herein refers to a straight- or branched-chain alkyl group from 1 to 20 carbon atoms in the chain. Exemplary alkyl groups include methyl, ethyl, vinyl, propyl, 10 isopropyl, butyl, isobutyl, sec-butyl, ter-butyl (tBu), pentyl isopentyl, tert-pentyl, hexyl, isohexyl, cetyl, tetraethyl, decyl or docecyl and the like.

The term “alcohol” as used herein is broadly interpreted to include alcohols of straight chain or branched alkyls. Examples include ethanol, n-propanol, isopropanol, tert-butanol, and the like.

15 The term “active” as used herein, for example “active metal” or “active sites”, refers to the metal or location of the catalyst on which a catalytic reaction occurs, such as propane dehydrogenation to propylene. Other non-active element or location of the catalyst serve as matrix or support of the active metals.

The term “metal”, “monometallic”, and “bimetallic” as used herein refers to the active 20 metal element of the catalyst, which may exist in the form of metal oxides within or thereon the catalyst matrix, wherein oxide refers to a metal-oxygen bond formed with the matrix or support of the catalyst.

The term “activity” as used herein refers to the conversion of propane to propylene, for example “higher activity” refers to the catalyst converting more propane to propylene.

25 The term “selectivity” as used herein refers to the preference of converting propane to propylene as compared to other side products, wherein propylene is the target product and anything else is considered as side products.

The term “stability” as used herein refers to the capacity of the catalyst to retain its inherent physiochemical and catalytic properties without undergoing degradation when subjected 30 to thermal conditions. For example, “thermal stability” refers to the catalyst retaining its morphology after higher temperature calcination, and advantageously confers longer catalytic conversion of propane to propylene without degradation.

The term "dispersed" as used herein refers to the spread of the active metal or heteroatom oxide on the matrix or support of the catalyst. For example, "highly dispersed" refers to a greater degree of spread of the metal and/or heteroatom oxide.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical
5 variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even
10 more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity, and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all
15 the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

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DESCRIPTION OF OPTIONAL EMBODIMENTS

Exemplary, non-limiting embodiments of a method of preparing a catalyst will now be disclosed.

25 The method of preparing a catalyst comprises the steps of:

- (a) adding a precursor of alumina, a precursor of heteroatom oxide, and one or more precursors of metals into a solution containing a surfactant to obtain a mixture;
- (b) filtering and/or drying the mixture of step a) to obtain a solid powder; and
- (c) calcining the solid powder obtained in step c) to obtain the catalyst.

30 Advantageously, the method may be used to synthesize catalysts using simple and readily available chemicals.

Further advantageously, the method may be used to synthesize catalysts with highly dispersed active metals sites. This is due to the specific composition of the precursors.

Still further advantageously, the method is facile and is easier to scale as no acid treatment is required.

The precursor of alumina used in the preparation of the catalyst may be aluminium isopropoxide, aluminium nitrate hexahydrate, or aluminium chloride hexahydrate.

5 Non-limiting examples of the heteroatom oxide dopant may be silicon dioxide (SiO_2). The heteroatom oxide may contain a heteroatom element of similar size (such as in terms of atomic radii) as compared to aluminium. The atomic radius of the heteroatom element may be closer to the atomic radius of aluminium. Therefore, the heteroatom oxide may form a homogeneous phase with the alumina (Al_2O_3) phase. The heteroatom oxide may form a bond
10 with the alumina.

The heteroatom may be silicon dioxide (SiO_2). Advantageously, silicon dioxide (SiO_2) may form a homogenous phase with alumina (Al_2O_3) through uniform oxide bonding, affording better doping and dispersion effects.

The precursor of the heteroatom oxide may be alkyl orthosilicate, metal isopropoxide, or
15 metal nitrate hexahydrate. The alkyl orthosilicate may be tetraethyl orthosilicate.

The metal may be selected from Group 9, 10, 11, 13, and 14 of the Periodic Table of Elements. The metal may be platinum (Pt), cobalt (Co), nickel (Ni), copper (Cu), gallium (Ga), tin (Sn), or their combinations thereof. Preferably, the monometallic metal may be cobalt (Co), nickel (Ni) or copper (Cu). Preferably, the bimetallic metal may be platinum (Pt)-M, whereby M
20 may be nickel (Ni), copper (Cu), tin (Sn), gallium (Ga), or their combinations thereof. Non-limiting examples of the bimetallic metal include Pt-Ni, Pt-Cu, Pt-Sn, Pt-Ga, or Ni-Cu.

In step (a), the precursor of alumina may be dissolved in the solvent at a molar concentration in the range of about 3 M to about 4 M, about 3.5 M to about 4 M, about 3 M to about 3.5 M or about 3.4 M to about 3.6M.

25 In step (a), the precursor of heteroatom oxide may be dissolved in the solvent at a molar concentration in the range of about 0.03 M to about 0.04 M, about 0.035 M to about 0.04M, about 0.03 M to about 0.035 M or about 0.034 M to about 0.046 M.

In step (a) the precursor of the active metal may be dissolved in the solvent at molar concentration of about 0.001 M to about 0.005 M, about 0.001 M to about 0.005 M, about 0.002
30 M to about 0.005 M, about 0.003 M to about 0.005 M, about 0.004 M to about 0.005 M, about 0.001 M to about 0.004 M, about 0.001 M to about 0.003 M, about 0.001 M to about 0.002 M or about 0.002 M to about 0.003 M.

Non-limiting examples of the surfactant may be alkyl amines, alkyl sulfate, or $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ (P123). The alkyl may be cetyl, deyl, or dodecyl. The alkyl sulfate may be sodium dodecyl sulfate. Advantageously, the surfactant may aid in the preparation of the alumina and/or heteroatom oxides (Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{TiO-Al}_2\text{O}_3$, etc) with high surface area (such as at least $300 \text{ m}^2/\text{g}$).

Non-limiting examples of the solvent include alcohols, water, or combinations thereof.

The solvent may be a combination of ethanol and water. The combination of ethanol and water may be at a volume ratio of about 60:40 to about 50:50.

The surfactant may be dissolved at a molar concentration in the range of about 0.01 M to about 0.45 M, about 0.05 M to about 0.45 M, about 0.1 M to about 0.45 M, about 0.15 M to about 0.45 M, about 0.2 M to about 0.45 M, about 0.25 M to about 0.45 M, about 0.3 M to about 0.45 M, about 0.35 M to about 0.45 M, about 0.4 M to about 0.45 M, about 0.01 M to about 0.4 M, about 0.01 M to about 0.35 M, about 0.01 M to about 0.3 M, about 0.01 M to about 0.25 M, about 0.01 M to about 0.2 M, about 0.01 M to about 0.15 M, about 0.01 M to about 0.1 M, or about 0.01 M to about 0.05 M.

The method may further comprise a step of stirring the solution of surfactant for a duration in the range of about 1 hour to about 2 hours, or until a transparent solution is obtained.

The method may further comprise a step of vigorously stirring the mixture of step (a) after step (a) but before step (b).

The mixture of step (a) may be stirred in the range of about 300 rotations per minute to about 600 rotations per minute.

The mixture of step (a) may be stirred at room temperature.

The mixture of step (a) may be stirred for a duration in the range of about 12 hours to about 72 hours, about 18 hours to about 72 hours, about 24 hours to about 72 hours, about 36 hours to about 72 hours, about 48 hours to about 72 hours, about 60 hours to about 72 hours, about 12 hours to about 60 hours, about 12 hours to about 48 hours, about 12 hours to about 36 hours, about 12 hours to about 24 hours, about 12 hours to about 18 hours.

In step (b), the mixture may be dried by heating in an oven.

In step (b), the mixture may be dried at a temperature in the range of about 40°C to about 100°C , about 50°C to about 100°C , about 60°C to about 100°C , about 70°C to about 100°C , about 80°C to about 100°C , about 90°C to about 100°C , about 40°C to about 90°C , about 40°C to about 80°C , about 40°C to about 70°C , about 40°C to about 60°C , or about 40°C to about 50°C .

In step (b), the mixture may be dried for a duration in the range of about 24 hours to about 72 hours, about 48 hours to about 72 hours, or about 24 hours to about 48 hours.

In step (b), the mixture may be dried until a solid dry powder is formed.

In step (c), the solid powder may be calcined at a temperature range of about 400 °C to about 600 °C, about 450 °C to about 600 °C, about 500 °C to about 600 °C, about 550 °C to about 600 °C, about 400 °C to about 550 °C, about 400 °C to about 500 °C, about 400 °C to about 450 °C.

The temperature may be reached at a ramping rate of about 0.5 °C per minute to about 2 °C per minute.

In step (c), the solid powder may be calcined for a duration in the range of about 4 hours to about 6 hours.

In step (c), the solid powder may be calcined under air atmosphere.

The method may further comprise, before adding step (a), the step (a1) of dissolving a precursor of alumina, a precursor of heteroatom oxide and one or more precursors of metal in a solvent to obtain a solution and a step (a2) of adding the solution of step (a1) into a solution of a surfactant to obtain a mixture.

Dissolving step (a1) may further comprise a step of adding an acid to the solution of dissolving step (a1); after dissolving step (a1) but before adding step (a2).

The acid may help with the dissolving of the precursor and the surfactant in the solvent. Non-limiting examples of the acid include nitric acid or hydrochloric acid. No sulfuric acid should be used for dissolving the precursor in the solvent, since sulfuric acid is not favorable to form the desired functional group versus the nitric acid or hydrochloric acid upon dissolving the surfactant. The acid may also help to dissolve the surfactant, for example, when the surfactant HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H (P123) is used. Direct addition of the acid to the P123 surfactant may cause degradation of the P123 surfactant, and therefore it is preferable to add the acid into the solution containing the precursor of alumina, the precursor of heteroatom oxide and the one or more precursors of metal, and then add the obtained mixture into the solution of the surfactant.

The acid may be added at a molar concentration in the range of about 0.01 M to about 0.05 M.

Exemplary, non-limiting embodiments of a catalyst will now be disclosed.

The catalyst comprises an alumina support with highly dispersed heteroatom oxide doping; and one or more highly dispersed metals within or thereon the alumina support.

The catalyst may have highly dispersed sites smaller than 2 nanometres, smaller than 3 nanometres, smaller than 4 nanometres, smaller than 5 nanometres, smaller than 6 nanometres, smaller than 7 nanometres, smaller than 8 nanometres, smaller than 9 nanometres, or smaller than 10 nanometres. The catalyst may have highly dispersed sites equal to or smaller than 2
5 nanometres. The highly dispersed sites are for active metal only and refer to less interaction with the neighbouring heteroatom.

The size of the highly dispersed sites may be in the range of about 1 nm to about 10 nm, about 2 nm to about 10 nm, about 3 nm to about 10 nm, about 4 nm to about 10 nm, about 6 nm to about 10 nm, about 8 nm to about 10 nm, about 1 nm to about 8 nm, about 1 nm to about 6
10 nm, about 1 nm to about 4 nm, about 1 nm to about 3 nm, about 1 nm to about 2 nm. The majority of the highly dispersed sites may have a size less than 2 nm.

The catalyst may have a dispersion of the one or more metals in the range of about 50% to about 80%, about 55% to about 80%, about 60% to about 80%, about 65% to about 80%, about 70% to about 80%, about 75% to about 80%, about 50% to about 75%, about 50% to about
15 70%, about 50% to about 65%, about 50% to about 60%, or about 50% to about 55%. The catalyst may have a dispersion of one or more metals around 80%. The dispersion is only for the active metals. Chemisorption measurement of the metals were performed using hydrogen and carbon dioxide (CO₂) as a probe molecule at 50 °C for 20 cycles with a volume of 0.334 millilitres.

20 Advantageously, the small, highly dispersed sites and high dispersion of the catalyst in the present disclosure may achieve high propane conversion activity around 40%, high selectivity around 98%, and high stability for 24 hours.

The weight of the heteroatom oxide may be in the range of about 1 weight% to about 20 weight%, about 3 weight% to about 20 weight%, about 5 weight% to about 20 weight%, about 7
25 weight% to about 20 weight%, about 10 weight% to about 20 weight%, about 15 weight% to about 20 weight%, about 1 weight% to about 15 weight%, about 1 weight% to about 10 weight%, about 1 weight% to about 7 weight%, about 1 weight% to about 5 weight% or about 1 weight% to about 3 weight%, based on the total weight of the catalyst. The weight of heteroatom oxide may be 10 weight% based on the total weight of the catalyst.

30 The heteroatom oxide dopant may be silicon dioxide (SiO₂).

The weight of one or more metals may be in the range of about 0.1 weight% to about 5 weight%, based on the total weight of the catalyst. The weight of the metal may be 0.1 weight% for Pt and others are less than or equal to 5 weight%, based on the total weight of the catalyst.

The remaining weight of the catalyst may be made up of the alumina, or a mixture of heteroatom oxide dopant and alumina.

Accordingly, the catalyst may have:

- i) the weight of the heteroatom oxide in the range of 1 wt% to 20 wt%; and
- 5 ii) the weight of the one or metals in the range of 0.1 wt% to 5 wt%,
based on the total weight of the catalyst,
and the alumina making up the remaining weight of the catalyst.

The surface area per gram of catalyst may be in the range of about 200 square metres per gram to about 400 square metres per gram. The pore volume may vary between about 0.2 cubic
10 metre per gram to about 0.5 cubic metre per gram. The surface area of the catalyst may be about 300 square metre per gram.

The present disclosure relates to a catalyst prepared according to the method as described herein.

Exemplary, non-limiting embodiments of a process of converting propane to propylene
15 will now be disclosed.

The process of converting propane to propylene comprises the step of heating a flow of propane in the presence of the catalyst as described herein. The heated flow of propane and the catalyst as described herein may be contacted in a reactor. Other catalytic processes, such as carbon dioxide hydrogenation, dry reforming of methane, and water gas shift reaction, may also
20 be possible using the catalyst as defined herein.

Advantageously, the process may produce propylene at 98% selectivity based on the amount of propane converted. Both monometallic and bimetallic catalyst may achieve high activity and high stability for propane dehydrogenation due to the highly dispersed distribution of the active sites on the catalyst.

25 Further advantageously, the process may stably convert propane to propylene for more than 24 hours without the need to stop the reaction to regenerate the catalyst. This is due to the highly dispersed active sites on the catalyst.

In the process, the catalyst may be provided on a fixed bed.

In the process, the weight of the catalyst may be in the range of about 0.1 gram to about
30 0.5 gram, about 0.2 gram to about 0.5 gram, about 0.3 gram to about 0.5 gram, about 0.4 gram to about 0.5 gram, about 0.1 gram to about 0.4 gram, 0.1 gram to about 0.3 gram, 0.1 gram to about 0.2 gram.

In the process, the heating may be done in a flow reactor.

In the process, the heating may be done at a temperature in the range of about 400 °C to about 600 °C, about 450 °C to about 600 °C, about 500 °C to about 600 °C, about 550 °C to about 600 °C, about 400 °C to about 550 °C, about 400 °C to about 500 °C, about 400 °C to about 450 °C.

5 In the process, the heating may be done for a duration in the range of about 1 hour to more than about 24 hours, about 6 hours to more than about 24 hours, about 12 hours to more than about 24 hours, about 18 hours to more than about 24 hours, about 1 hour to about 18 hours, about 1 hour to about 12 hours or about 1 hour to about 6 hours.

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BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of limits of the invention.

15 **Fig. 1** shows a spectrum of Extended X-Ray Absorption Fine Structure (EXAFS) of catalysts prepared according to Example 1 below using different aluminium precursors. The y-axis is the Fourier Transform (FT) magnitude.

Fig. 2 shows an EXAFS spectrum of catalysts prepared according to Example 1 using different heteroatom oxide precursors. The y-axis is the FT magnitude.

20 **Fig. 3** shows (a) percentage conversion and (b) percentage selectivity graphs of the process of converting propane to propylene using the catalyst prepared according to Example 1 with different amounts of heteroatom oxide.

Fig. 4 shows (a, b) High Resolution Transmission Electron Microscope (HRTEM) images of a catalyst prepared according to Example 1, with a magnification of 50,000× resolution; (c) a Scanning Transmission Electron Microscope (STEM) image of the catalyst with a scale bar of 5 nm, and (d) a diagram of CO *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of the catalyst.

Fig. 5 shows an EXAFS spectrum of a catalyst prepared with a using nickel (Ni) metal instead of cobalt (Co) according to Example 1.

30 **Fig. 6** shows (a) CO-DRIFTS spectra and (b) Temperature Programmed Reduction (TPR) diagrams of various catalysts prepared according to Example 1 for monometallic catalyst and Example 2 for bimetallic catalyst.

Fig. 7 shows the conversion and selectivity performances of a bimetallic catalyst prepared according to Example 2 for use in a process of converting propane to propylene.

Fig. 8 shows the carbon monoxide (CO) chemisorption spectra for 20 cycles of a monometallic catalyst prepared according to Example 1 and a bimetallic catalyst prepared according to Example 2.

EXAMPLES

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Method A of Synthesizing a Catalyst

Herein, alkyl amines were used as a templating agent, metal isopropoxide was used as Al, Ti and Zr precursors, tetraethyl orthosilicate was used as a silica precursor, while ethanol and water were used as a solvent. Alkyl amines, tetraethyl orthosilicate (TEOS) and aluminum isopropoxide were purchased from Sigma Aldrich (St. Louis, Missouri, United States) and used as is. Absolute ethanol was purchased from VWR chemical (Radnor, Pennsylvania, United States) and used as is. The heteroatom doped alumina oxide was prepared in an ethanolic solution consisting of 55% ethanol and 45% water by volume, with a total volume of 65 milliliters. Subsequently, 0.02 moles of alkyl amine (dodecylamine) were added into the ethanolic solution. The mixture was stirred until a transparent solution was obtained. Post this step, all the metal, heteroatom oxide, and alumina precursors were added in a desired quantity to obtain 5 weight% metal, 10 weight% heteroatom oxide and 85 weight% alumina (Al_2O_3). The desired quantity may be 2 to 4 grams of surfactant, 3 to 4 grams of aluminium isopropoxide, 0.3 to 0.4 grams of tetraethyl orthosilicate and different amounts of active metal precursors depending on the oxidation state of the desired element and can be calculated using mole balance. For example, where the catalyst is 5 wt% Co in 1 g of support, 0.5 g of cobalt (II) nitrate hexahydrate was used. The mixture was stirred for 24 hours at room temperature under vigorous stirring (300 to 600 revolutions per minute) and then filtered to obtain the residue, and the excess supernatant was removed via the means of vacuum filtration. The precipitant was dried in a vacuum oven at 100 °C and calcined at 600 °C for 4 hours with the ramping rate of 1 °C per minute.

Monometallic catalyst samples such as those containing cobalt, nickel and copper were synthesized using method A.

Example 2: Method B of Synthesizing a Catalyst

5 In this method, Pluronic P123 was used as a structure directing agent. 2 grams of P123 (purchased from Sigma Aldrich of St. Louis, Missouri, United States) was added to 40 milliliters of ethanol. The mixture was stirred for 2 hours until the Pluronic P123 was completely dissolved. In another beaker, the desired precursors, such as aluminium isopropoxide, tetraethyl orthosilicate and metal nitrate hexahydrates were added to 20 milliliters of ethanol. Metal nitrate
10 hexahydrates were purchased from Sigma Aldrich (St. Louis, Missouri, United States) and used as is. For 5 weight% metal loading, 3.6 grams of aluminium isopropoxide, 0.4 grams of tetraethyl orthosilicate (TEOS) and 0.5 g of metal nitrate were added. Nitric acid (0.03 M, purchased from Alfa Aesar of Haverhill, Massachusetts, United States) or hydrochloric acid (0.03M, purchased from Alfa Aesar of Haverhill, Massachusetts, United States) was then added
15 for the complete dissolution of metal precursors. The solution was kept under stirring for 2 hours and then it was added to the solution containing Pluronic P123 and ethanol. The total mixture was then stirred for 12 hours and dried in oven at 60 °C for an additional 48 hours. After drying, the solid powder was calcined at 600 °C for 4 hours under air atmosphere with 1 °C per minute ramping rate. In this investigation, the types of heteroatom oxide dopant used, such as Ti, Zr, and
20 Si, were varied, to find the best resulting doping element and composition of each heteroatom. Additionally, the alumina precursor used was varied, for example, aluminium nitrate hexahydrate and aluminium chloride hexahydrate were also used, apart from aluminium isopropoxide.

Monometallic catalyst samples such as those containing cobalt, nickel and copper were
25 also synthesized using method B. Bimetallic catalyst samples were prepared using method B.

Example 3: Characterization of the Catalysts

Characterization techniques, such as Extended X-Ray Absorption Fine Structure (EXAFS), Carbon Monoxide *in situ* Diffuse Reflectance Infrared Fourier Transform
30 Spectroscopy (CO-DRIFTS), Scanning Transmission Electron Microscopy (STEM), and High Resolution Transmission Electron Microscopy (HRTEM), were conducted to confirm the formation of highly dispersed monometallic and bimetallic sites. X-Ray Absorption Fine Structure (EXAFS). The analysis was performed at Singapore Synchrotron Light Source

facilities. For each calcined samples 30 mg was mixed with 70 mg boron nitride as a reference and made into pellet form. The Co K edge was measured and analyzed using Athena Package. The morphology, and particle size and dispersion are visually observed using High-Resolution Transmission electron microscopy (HRTEM) images were recorded by JEOL JEM-2100 F system. and Scanning Transmission Electron Microscope (STEM). A small fraction of sample was dispersed in alcohol solution and ultra-sonicated for more than an hour before the analysis was done and the sample was dispersed in a copper grid. Diffuse Reflectance Fourier Transform Infrared (DRIFTS) Spectroscopy: The analysis was performed in Bruker FTIR Vertex 70 spectrometer using Harrick Praying Mantis DRIFTS gas cell equipped with ZnSe windows and a controlled gas system capable of carrying out a reaction at the higher temperature. The in-situ CO DRIFTS was performed using diluted CO as probe gas molecule. Prior to the analysis the catalyst was pretreated at 550 °C under inert atmosphere to remove surface impurities and water absorbed by the sample. After the pretreatment for 1 hour, the reactor was cooled down to 50 °C under helium and purged for 30 min. The gas was then switched to CO and helium. The CO was adsorbed until saturation for 1 hour during which the spectra was collected for the analysis. The data curation was performed using OPUS software.

EXAFS analysis was used to determine the formation of highly dispersed sites. Optimization of the high surface area and porosity of the alumina was first conducted using three different aluminium precursors, namely, aluminium isopropoxide, aluminium chloride, and aluminium nitrate. Herein, metal oxide (cobalt) and heteroatom oxide (SiO_2) were doped as a model compound and the EXAFS spectra are shown in Fig. 1. As seen in Fig. 1, only Co- SiO_2 - Al_2O_3 (3 weight% Co, 10 weight% Si, 87 weight% Al_2O_3) using aluminium isopropoxide precursor afforded a well-dispersed cobalt oxide formation, while the other two aluminium precursors failed to form the highly dispersed sites. The availability of a long chain molecule and micelle formation along with the aluminium isopropoxide precursor may be the reason for the high dispersion of cobalt oxide.

In another investigation, the effect of different heteroatom oxide dopant, such as Si, Ti, and Zr, were identified. Fig. 2 shows the EXAFS spectra demonstrating the effect of varying the heteroatom oxide dopant. The catalysts that were used in Fig. 2 comprised of 5 weight% Co, 10 weight% heteroatom oxide and 85 weight% Al_2O_3 based on the total 1 gram of the catalyst. Referring to Fig. 2, the single peak at 1-2 Angstrom was attributed to the Co-O bond, whereas the two twin peaks between 2-3 Angstrom and 5 Angstrom were attributed to the spinel structure of cobalt ions. A single peak at 1-2 Angstrom and the absence of twin peaks for Co- SiO_2 - Al_2O_3

(5 weight% Co, 10 weight% Si, 85 weight Al₂O₃) indicated that most of the cobalt were well-dispersed in the aluminosilicate matrix as cobalt oxide, where Co(II) oxidation state was the most active phase for the dehydrogenation reaction. Comparatively, both Ti and Zr heteroatom oxide dopants showed the presence of cobalt spinel structure within their mixed alumina matrix, as seen from the presence of twin peaks at 2-3 Angstrom and 5 Angstrom.

The amount of silicon dioxide was also varied and its effect on propane dehydrogenation is shown in Fig. 3. The Co-10SiO₂-Al₂O₃ (3 weight% Co, 10 weight% Si, 87 weight% Al₂O₃) had the highest conversion and for propane to propylene across the 10 hours of the dehydrogenation reaction.

Additional characterization techniques which support the formation of highly dispersed sites are shown in Fig. 4a to 4d. In Fig. 4a to 4c, the Co-SiO₂-Al₂O₃ catalyst is provided as described herein, comprising 3 weight% Co, 10 weight% SiO₂ and 87 weight% Al₂O₃ based on the total 1g of the catalyst. In Fig. 4d, the Cu-Al₂O₃ catalyst is provided as described herein, comprising 3 weight% Cu and 97 weight% Al₂O₃ based on the total 1 gram of the catalyst; the Cu-SiO₂-Al₂O₃ catalyst is provided as described herein, comprising 3 weight% Cu, 10 weight% SiO₂ and 87 weight% Al₂O₃ based on the total 1 gram of the catalyst.

In Fig. 4a, the HRTEM image of Co-SiO₂-Al₂O₃ with optimized silicon dioxide content, showed highly dispersed cobalt in the ordered mesoporous alumina. The highly dispersed sites of cobalt are shown in the HRTEM images of Fig. 4b and in the STEM images of Fig. 4c. The white circles indicate the active sites present in the support or it also signifies the small size of the active site in the scale of 20 nm and 5 nm. Fig. 4d shows the CO-DRIFTS profile for Cu-Al₂O₃ and Cu-10SiO₂-Al₂O₃. The CO-DRIFT profile for Cu-Al₂O₃ shows two peaks; one peak at 2116 cm⁻¹ and another peak at 2100 cm⁻¹, which were assigned to the interaction of linear carbon monoxide (CO) molecules with the copper nanoparticles. The CO-DRIFTS profile for Cu-10SiO₂-Al₂O₃ shows a single sharp peak which indicates that the copper was highly dispersed and low coordinated with silicon dioxide dopant in alumina. The interaction between the CO molecule and the copper phase determines the dispersion of copper oxide in the catalysts. This analysis revealed that there was a more uniform distribution of smaller copper particle size after doping Cu-Al₂O₃ with SiO₂.

Fig. 5 describes another example of highly dispersed metal catalysts Ni-SiO₂-Al₂O₃ (5 weight% Ni, 10 weight% SiO₂, 85 weight% Al₂O₃ based on the total 1 gram of the catalyst). The EXAFS spectra also showed a single distinguishable peak located between 1-2 Angstroms, thereby confirming the formation of highly dispersed sites of nickel (Ni).

Bimetallic catalyst samples were also prepared using the same methodology described herein, whereby Pt-Cu, Pt-Ni, Ni-Cu, or Pt-Ga were doped onto the silicon dioxide doped alumina matrix ($\text{-SiO}_2\text{-Al}_2\text{O}_3$). The composition of the bimetallic catalysts comprised of 0.1 weight% Pt, 3 weight% Cu/Ni/Ga, 10 weight% SiO_2 , and 87 weight% Al_2O_3 based on the total 1 gram of catalyst. The highly dispersed state of the bimetallic catalysts was confirmed using CO-DRIFTS and hydrogen Temperature Programmed Reduction (H_2 -TPR). In Fig. 6a, the Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is provided as described herein, comprising 3 weight% Cu, 10 weight% SiO_2 and 87 weight% Al_2O_3 based on the total 1 gram of the catalyst; the Pt-Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is provided as described herein, comprising 0.1 weight% Pt, 3 weight% Cu, 5 weight% SiO_2 and 92 weight% Al_2O_3 based on the total 1 gram of the catalyst. In Fig. 6b, the Pt-Ni- $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is provided as described herein, comprising 0.1 weight% Pt, 5 weight% Ni, 5 weight% SiO_2 and 90 weight% Al_2O_3 based on the total 1 gram of the catalyst; the Pt-Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is provided as described herein, comprising 0.1 weight% Pt, 3 weight% Cu, 5 weight% SiO_2 and 92 weight% Al_2O_3 based on the total 1 gram of the catalyst; the Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is provided as described herein, comprising 3 weight% Cu, 10 weight% SiO_2 and 87 weight% Al_2O_3 based on the total 1 gram of the catalyst. In Fig. 6a, a single peak at $\sim 2110\text{ cm}^{-1}$ indicated the formation of highly dispersed sites for both monometallic (Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$) and bimetallic (Pt-Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$) catalysts. In addition, the TPR profile shown in Fig. 6b consisted of one sharp peak at about 400 °C, 390 °C and 260 °C for Pt-Ni- $\text{SiO}_2\text{-Al}_2\text{O}_3$, Pt-Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$, respectively, for both the monometallic and bimetallic catalysts. The single peak at low temperature also indicated a well-dispersed uniform alloy of Pt with Cu and/or Ni.

Fig. 7 refers to the performance of the bimetallic catalyst Pt-Cu- $\text{SiO}_2\text{-Al}_2\text{O}_3$ (0.1 weight% Pt, 3 weight% Cu, 10 weight% SiO_2 , 87 weight% Al_2O_3 based on the total 1 gram of the catalyst) for propane dehydrogenation. The propane dehydrogenation reaction was carried out at a temperature of 550 °C, with a gas feed stream consisting of 10 volume% propane and 10 volume% hydrogen and 80 volume% inert gas (helium or nitrogen gas); the total flow rate of the feed gas was 20 milliliters per minute and propane flow rate was 2 milliliters per minute. The reactor was maintained at atmospheric pressure. The bimetallic catalyst was mounted inside a quartz tube micro-reactor with internal diameter of 4 millimeters and bed height of 2 centimeters. The catalyst was kept within the center of the heating zone (heating zone length of 5-7 centimeters). It was found that there was a 40% propane conversion with a 98% selectivity to propylene when operated at reaction conditions described herein. The stability of the bimetallic catalysts was measured over 24 hours of propane dehydrogenation. The catalyst showed

negligible deactivation, with only a small fraction of coke formation after 24 hours (not shown). The advantage of using a simple one-step approach to synthesize monometallic and bimetallic catalysts can be seen from their promising performance of high activity, high selectivity, and high stability toward propane dehydrogenation. The method described herein is also scalable and could be applied for other high temperature reactions, including carbon dioxide hydrogenation, dry reforming of methane, and water gas shift reactions.

Fig. 8 shows the chemisorption of carbon monoxide on Cu-SiO₂-Al₂O₃ and Pt-Cu-SiO₂-Al₂O₃. The measurement was done at 50 °C for 20 cycles. Based on the CO chemisorption spectra, the dispersion of copper in Cu-SiO₂-Al₂O₃ was 54%, and the dispersion of Pt obtained in Pt-Cu-SiO₂-Al₂O₃ was 76.6% with a copper dispersion of close to 50% in the Pt-Cu-SiO₂-Al₂O₃ catalyst.

Summary of Examples

The combination of alumina, heteroatom oxide, surfactant and one or more metals as described by the methods herein enables the production of a catalyst with highly dispersed mono or bimetallic metal sites that demonstrates high propane conversion activity of 40% and high propylene selectivity of 98%. The performance of said catalyst can be attributed to the high dispersion of one or more metals as supported by the EXAFS, HRTEM, CO-DRIFTS and H₂-TPR data provided herein.

INDUSTRIAL APPLICABILITY

In the present disclosure, the catalyst prepared from the method described herein may be used for propane dehydrogenation. The ease of preparation of said catalyst from the method as described further allows the catalyst to be used on a large scale to convert propane to propylene.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading this foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

1. A method of preparing a catalyst comprising the steps of:
 - (a) adding a precursor of alumina, a precursor of heteroatom oxide and one or more precursors of metal into a solution of a surfactant to obtain a mixture;
 - (b) filtering and/or drying the mixture of step a) to obtain a solid powder; and
 - (c) calcining the solid powder of step b) to obtain the catalyst.
2. The method of claim 1, comprising the step of selecting said precursor or alumina from an aluminium isopropoxide, an aluminium nitrate hexahydrate or an aluminium chloride hexahydrate.
3. The method of claim 1 or 2, comprising the step of selecting said precursor of heteroatom oxide from alkyl orthosilicate.
4. The method of any one of claims 1 to 3, comprising the step of selecting the metal of said one or more precursors of metal from Groups 9, 10, 11, 13 and 14 of the Periodic Table.
5. The method of claim 4, comprising the step of selecting the metal of said one or more precursors of metal from the group consisting of cobalt (Co), nickel (Ni), platinum (Pt), copper (Cu), gallium (Ga), tin (Sn) and combinations thereof.
6. The method of any one of claims 1 to 5, comprising the step of selecting the surfactant from the group consisting of alkyl amines, alkyl sulfate and $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ (P123).
7. The method of any one of claims 1 to 6, further comprising the step of:
 - (a1) dissolving a precursor of alumina, a precursor of heteroatom oxide and one or more precursors of metal in a solvent to obtain said solution;
 - (a2) adding the solution of step (a1) into a solution of surfactant to obtain a mixture; and
 - (a3) vigorously stirring the mixture of step (a2) after step (a2) but before step (b).
8. The method of claim 7, further comprising the step of adding an acid to the solution of step (a1), wherein said acid is nitric acid or hydrochloric acid.
9. The method of claim 7, wherein said stirring is undertaken at a stirring rate in the range of 300 rpm to 600 rpm.
10. The method of any of claims 1 to 9, wherein said filtering in step (b) is vacuum or gravity filtration.

11. The method of any one of claims 1 to 10, wherein said drying in step (b) is undertaken at a temperature in the range of 40 °C to 100 °C under air atmosphere.
12. The method of any one of claims 1 to 11, wherein said calcining in step (c) is undertaken at a temperature range of 400 °C to 600 °C under air atmosphere.
- 5 13. A catalyst, comprising
an alumina support with highly dispersed heteroatom oxide doping; and
one or more metals highly dispersed within or thereon said alumina support.
14. The catalyst of claim 13, comprising a plurality of highly dispersed sites having sizes smaller than 10 nm.
- 10 15. The catalyst of claim 13 or 14, wherein the dispersion of said one or more metals is in the range of 50% to 80%.
16. The catalyst of any one of claims 13 to 15, wherein:
- i) the weight of said heteroatom oxide is in the range of 1 wt% to 20 wt%;
and
- 15 ii) the weight of said one or more metals is in the range of 0.1 wt% to 5 wt%,
based on the total weight of the catalyst,
and the alumina makes up the remaining weight of the catalyst.
17. A process of converting propane to propylene comprising the step of heating a flow of propane in the presence of the catalyst of any one of claims 13 to 16.
- 20 18. The process of claim 17, wherein said heating step is undertaken at a temperature in the range of 400 °C to 600 °C.