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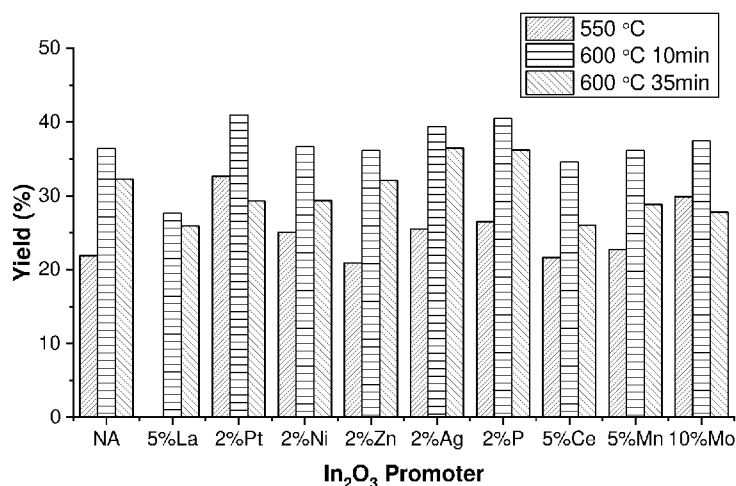
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(54) Title: A CATALYST COMPOSITION

[Fig. 5]



(57) Abstract: The present invention relates a catalyst composition comprising metal oxides useful in a catalytic oxidative dehydrogenation of the short chains of alkene into its corresponding diene, in particular, the catalytic oxidative dehydrogenation of 1-butene to 1,3-butadiene (BD). In a preferred embodiment, the catalyst is indium oxide (In_2O_3) supported on alumina (Al_2O_3) and optionally promoted by diphosphorus pentoxide (P_2O_5) and/or platinum (Pt). The present invention also relates to a method for preparing the catalyst composition as defined herein.

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Description

A Catalyst Composition

Cross-Reference to Related Application

This application claims priority to Singapore application number 10201805560P filed on 27 June 2018, the disclosure of which is hereby incorporated by reference.

Technical Field

The present invention generally relates to a catalyst composition comprising metal oxides useful in a catalytic oxidative dehydrogenation of the short chains of alkene. The present invention is also directed to a method for preparing the catalyst composition as defined herein.

Background Art

1,3-butadiene (or abbreviated as “BD”) is regarded as one of the important bulk chemicals with myriads of applications, in particular in the manufacture of polymers. The examples of polymers that can be prepared from 1,3-butadiene include styrene butadiene rubber (SBR), polybutadiene rubber (PB), styrene-butadiene latex (SBL) and acrylonitrile-butadiene-styrene (ABS) resin. Today, 1,3-butadiene is primarily synthesized via steam cracking of hydrocarbon feedstock, as a by-product in C4 fraction.

However, due to the limited resources of crude oil and the vast reserves of gases, particularly shale gas, the cracking feedstock has been gradually shifting from naphtha to gases. This change results in a significant decrease of the production of 1,3-butadiene in the cracking products, from about 15 to 20% to about 1 to 5%. The global 1,3-butadiene market is still increasingly in demand and it is predicted to be expanding continuously in the future. Alternative processes, such as those that are environmentally friendly, are thus required to meet the increasing demand.

Among the alternative processes available today, at least two (2) methods are widely used to produce 1,3-butadiene i.e. a) dehydrogenation of 1-butene; and b) oxidehydrogenation of 1-butene with oxygen. In the former, it is known that the thermodynamic equilibrium is low. For instance, at approximately 0.1 bar, the equilibrium conversions for the dehydrogenation reaction are reported to be 35% and 71% at 500°C and 600°C, respectively. Hence, such process operates at relatively low conversion (about 40 to 50%) and selectivity (about 70 to 90%). Other limitations of this process include short on-stream periods to avoid the formation of the coke on the catalysts, which must be then regenerated and release of steam from the process.

The latter process, although being regarded as a better method than the former in view of low energy consumption and suppression of coke deposition, the oxidehydrogenation of 1-butene with oxygen exhibits low selectivity, partly because of strong oxidative capacity. Additionally, the mixture ratio in the reaction is restricted in light of the inherent explosive risk of this process.

In light of the above, the present invention therefore provides a catalyst composition used in a catalytic oxidative dehydrogenation (ODH) that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

5 In one aspect, there is provided a catalyst composition comprising:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

10 Advantageously, when used in a chemical reaction, the catalyst composition as defined herein may enhance the selectivity of the reaction thereby minimizing the side reactions and the formation of side products.

Further, said catalyst composition may also advantageously increase the yield of the reaction at a relatively lower reaction temperature.

15 Yet advantageously, the catalyst composition as defined herein may be stable and may remain highly active after being used in the reaction.

In another aspect, there is provided a method of preparing a catalyst composition comprising the steps of:

- a) adding a support to at least one metal precursor dissolved in a solvent or a mixture of solvents;
- 20 b) drying the mixture obtained in step a) at a drying temperature; and
- c) heating the dried mixture obtained in step b).

In another aspect, there is provided a process of converting an alkene to a diene comprising the step of

25 exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C;

wherein said catalyst composition comprises:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

30 Definitions

The following words and terms used herein shall have the meaning indicated:

35 The term "alkene" as used herein refers to a hydrocarbon compound comprising one carbon-to-carbon double bond. Unless specified otherwise, the term "alkene" used in the present disclosure may be acyclic alkene having only one carbon-to-carbon double bond and no other functional groups. Such alkene may therefore be termed as mono-ene.

The term "diene" as used herein refers to a compound having two carbon-to-carbon double bonds. Accordingly, the term "1,3-diene" refers to a compound having two carbon-to-carbon double bonds where these double bonds are in the 1,3-position.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical 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 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 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.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

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

There is provided a catalyst composition comprising:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

The present disclosure also provides a catalyst composition consisting essentially of:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

The metal of the at least one metal oxide of the catalyst composition as defined herein may be a transition metal, a non-transition metal, a combination thereof or an alloy thereof. Non-limiting examples of the transition metals include titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), zirconium (Zr), zinc (Zn), or a combination thereof
5 or an alloy thereof. It is to be understood that other transition metals than those shown above may also be used. Transition metals referred herein are the transition metals found in Group IIIB, IVB, VB, VIB, VIIB, VIII, IB or IIB of the Periodic Table.

Non-transition metals may be selected from other metals found in the Periodic Table, which do not form part of the transition metals above. Such non-transition metals may be alkali metals
10 and alkaline earth metals. Non-limiting examples of such non-transition metals include aluminium (Al), cadmium (Cd), indium (In), tin (Sn), lead (Pb), thallium (Tl), bismuth (Bi), a combination thereof or an alloy thereof. It is to be understood that other non-transition metals than those shown above may also be used. Preferred metal of the at least one metal oxide of the catalyst composition may be indium (In).

Accordingly, when the metal of the at least one metal oxide in the catalyst composition as defined above is the transition metal, the metal oxide may therefore be termed as transition metal oxide. Such transition metal oxide may be selected from the group consisting of TiO_2 , VO_2 , V_2O_5 , CrO , Cr_2O_3 , MnO , Mn_2O_3 , Mn_3O_4 , Mn_2O_7 , CoO , Co_2O_3 , Co_3O_4 , NiO , Ni_2O_3 , ZrO_2 , ZnO , a combination thereof and an alloy of such oxides. For the non-transition metal, the metal
15 oxide may be selected from the group consisting of Al_2O_3 , CdO , In_2O_3 , SnO_2 and PbO , a combination thereof and an alloy of such oxides. The at least one metal oxide may also be a combination of a transition metal oxide with a non-transition metal oxide, which may be in the form of an alloy or a mixture thereof.

The promoter of the catalyst composition as defined above may facilitate the catalytic process
25 when said catalyst composition is used in a chemical reaction or transformation, that is, the promoter may enhance the yield of the reaction, increase the selectivity of the reaction or confer other benefits that cannot be obtained if such promoter is absent.

The promoter as defined above may be an oxide of a non-metal element, a metal including transition metal, non-transition metal or mixtures thereof. Non-limiting examples of the oxide of
30 a non-metal element include P_2O_5 , P_4O_6 , As_2O_5 , Sb_4O_6 , SeO_2 , SeO_3 , Bi_2O_3 , TeO_2 , or TeO_3 .

As stated above, the transition metal may also be used as the promoter. Non-limiting examples of such transition metal may be as defined in the previous section. However, it should be noted that the examples of the transition metal are not limited to those examples and therefore may also extend to other transition metals found in Group IIIB, IVB, VB, VIB, VIIB, VIII, IB or IIB
35 of the Periodic Table.

Additionally, the promoter may also be an alkali or alkaline earth metal such as sodium (Na), potassium (K), calcium (Ca), or barium (Ba). Further, the promoter as defined herein may also include both the oxide of a non-metal element and a transition metal. Preferred promoter in the present disclosure is P_2O_5 and platinum (Pt).

When more than one promoter is used, such as in exemplified embodiment above where both P_2O_5 and platinum are used as promoters, each of the promoters may then be termed as a first promoter, a second promoter, a third promoter and so forth. In the above example, P_2O_5 may be regarded as the first promoter and platinum (Pt) as the second promoter or vice versa. More
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importantly, the presence of one or more promoter in the catalyst composition may provide synergistic effect to the catalyst composition.

Hence, the present disclosure also provides a catalyst composition comprising:

- a. at least one metal oxide;
- 5 b. at least one promoter; and
- c. a support.

The present disclosure further provides a catalyst composition consisting essentially of:

- a. at least one metal oxide;
- b. at least one promoter; and
- 10 c. a support.

Advantageously, when used in a chemical reaction, the catalyst composition as defined herein may enhance the selectivity of the reaction thereby minimizing the side reactions and the formation of side products. Further, said catalyst composition may also advantageously increase the yield of the reaction at a relatively lower reaction temperature.

15 The support of the catalyst composition as defined herein may be thermally and/ or chemically stable. Moreover, said support of the catalyst composition may be able to withstand process conditions required to prepare or activate pre-catalysts. For instance, if heat treatment such as heating is required in the preparation of the pre-catalysts, the catalyst support used is thermally stable.

20 The support of the catalyst composition as defined above may provide high surface areas useful in heterogeneous catalytic process. Non-limiting examples of the support of the catalyst composition include alumina (Al_2O_3), silica, TiO_2 , ZrO_2 , zeolite, microporous and mesoporous materials or mixtures thereof. As used herein, the mesoporous material refers to a material having pore size with diameter between 2 nm to 50 nm and the microporous material refers to a
25 material having pore size with diameter less than 2 nm. The metal used as the catalyst support may be as previously defined. Hence, such metal may be selected from the transition metal, non-transition metal, a combination thereof and an alloy thereof. In a preferred embodiment, the support is Al_2O_3 .

The catalyst composition as defined herein may be useful in chemical reactions involving
30 starting materials such as alkanes, alkenes, alcohols and related compounds, where the short-chained alkanes or short-chained alcohols may have 1 to 6 carbon atoms and the short-chained alkenes may have 2 to 6 carbon atoms. Non-limiting examples of the reactions, in which the catalyst composition as disclosed herein may be used, include oxidative dehydrogenation of the short chains of alkene. In an embodiment, the oxidative dehydrogenation of the short chains of
35 alkene disclosed herein may produce corresponding dienes. In a preferred embodiment, the catalyst composition as defined herein may be used in the oxidative dehydrogenation of 1-butene to produce 1,3-butadiene.

Therefore, additionally there is also provided a catalyst composition comprising:

- a. indium oxide (In_2O_3);
- 40 b. Pt and P_2O_5 as promoters; and
- c. Al_2O_3 as catalyst support.

As an exemplary embodiment, the present disclosure provides a catalyst composition consisting essentially of:

- a. indium oxide (In_2O_3);
- b. Pt and P_2O_5 as promoters; and
- c. Al_2O_3 as catalyst support.

In the presence of the catalyst composition as defined herein, the conversion of 1-butene to valuable chemicals such as 1,3-butadiene may be carried out in the presence of an oxidant such as oxygen, carbon dioxide or a mixture thereof. Other suitable oxidants than the above may also be used as appropriate. Use of a soft oxidant (for instance carbon dioxide) has several benefits over molecular oxygen including minimization of total oxidation, reduction of hot spots as well as being environmentally benign. Hence, the preferred oxidant used in the present disclosure is carbon dioxide.

Advantageously, the catalyst composition as defined herein may be stable and remain highly active after being used in the reaction i.e. one or more cycles of reaction. Therefore, when desired, it may be possible to regenerate said catalyst composition to be used for a further cycle of reaction.

The catalyst composition as defined herein may comprise active components or ingredients or constituents that may determine the catalytic performance of said catalyst composition. Such active ingredients may therefore be termed as active catalytic ingredients. The active catalytic ingredients of the catalyst components described above may be metal oxide(s) and/ or promoter(s). Hence, the active catalytic ingredients may therefore refer to the catalyst composition excluding or in the absence of the catalyst support.

As an exemplary embodiment, for a catalyst composition consisting essentially of:

- a. indium oxide (In_2O_3);
- b. Pt and P_2O_5 as promoters; and
- c. Al_2O_3 as catalyst support;

the active catalytic ingredients of the above catalyst composition are indium oxide (In_2O_3) and promoters (Pt and P_2O_5).

When used in the chemical reaction, the active catalytic ingredients of the catalyst composition as defined above may be present in an amount ranging from about 0.01 wt.% to about 60 wt.%, for example about 0.05 wt.%, about 0.1 wt.%, about 0.5 wt.%, about 1 wt.%, about 2 wt.%, about 5 wt.%, about 8 wt.%, about 10 wt.%, about 20 wt.%, about 25 wt.%, about 25.5 wt.%, about 26 wt.%, about 27 wt.%, about 28 wt.%, about 30 wt.%, about 32 wt.%, about 35 wt.%, about 40 wt.%, about 45 wt.%, or about 50 wt.%, based on the weight of the catalyst composition. For clarity, when the active catalytic ingredients are metal oxide(s), the amount above corresponds to the amount of the metal oxide(s) present in the catalyst composition. However, when the active catalytic ingredients consist essentially of the metal oxide(s) and at least one promoter, the amount above corresponds to the total amount of the metal oxide(s) and the at least one promoter present in the catalyst composition.

The amount of the at least one metal oxide in the catalyst composition may be in a range of about 5 wt.% to about 50 wt.% of the total weight of the catalyst composition, such as about 5 wt.%, about 10 wt.%, about 15 wt.%, about 20 wt.%, about 25 wt.% and about 50 wt.%.

5 The promoter of the catalyst composition as defined herein may be present in the amount ranging from 0 wt.% to about 20 wt.% of the total weight of the catalyst composition, such as 0 wt.%, about 1 wt.%, about 2 wt.%, about 3 wt.%, about 5 wt.%, about 10 wt.%, about 15 wt.% and about 20 wt.%. It should be noted that the range shown above may also be applicable when more than one promoter is used. Hence, the above range may refer to the total amount of the promoters used. For clarity and avoidance of doubt, when promoters A and B are present, the
10 total amount of these two promoters (sum of amount of A and B) may be in a range of 0 wt.% to about 20 wt.% of the total weight of the catalyst composition.

The amount of the support (also termed as “catalyst support”) available in the catalyst composition may be derived from the amount of the at least one metal oxide and the promoter, which altogether make up 100 wt.% of the catalyst composition. For avoidance of doubt, if the
15 at least one metal oxide is present at about 15 wt.% and there is only one promoter being used of about 3 wt.%, it then follows the amount of the catalyst support is about 82 wt.%.

When used in the oxidative dehydrogenation of 1-butene to produce 1,3-butadiene (BD), the reaction may be undertaken at the temperature of about 450°C to about 700°C, such as about 500°C, about 525°C, about 550°C, about 575°C, about 600°C, about 625°C, about 650°C, and
20 about 700°C.

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

The present disclosure provides a method of preparing the catalyst composition as defined herein comprising the steps of:

- 25 a) adding a support to at least one metal precursor dissolved in a solvent or a mixture of solvents;
b) drying the mixture obtained in step a) at a drying temperature; and
c) heating the dried mixture obtained in step b).

30 The solvent used in the method as defined herein may include aqueous solvent, organic solvent or a mixture thereof. More importantly, the at least one metal precursor should be dissolved or substantially dissolved in said solvent. Non-limiting examples of the organic solvent to dissolve the at least one metal precursor include methanol, ethanol, acetone, 1,2-dichloroethane, acetonitrile, dimethylformamide (DMF). Other suitable organic solvents that are not shown above may also be used. The aqueous solvent used in the above method may be water.

35 The drying temperature in step b) may be from about 50°C to 120°C, such as about 60°C, about 70°C, about 80°C, about 90°C, about 100°C or about 110°C.

The drying process in step b) may be undertaken for a period ranging from about 1 hour to about 20 hours such as about one hour, about 2 hours, about 3 hours, about 5 hours, about 10 hours, or about 20 hours.

The drying process in step b) may be repeated when desired with the same or different drying temperature and duration. In an embodiment, the drying in step b) comprises drying at about 50°C and a further drying at about 110°C for approximately 12 hours.

Further, it is to be noted that the objective of the drying process above is to substantially remove the solvent prior to the heating process of step c).

The heating process in step c) may be undertaken under a heating temperature ranging from about 400°C to 800°C, such as about 450°C, about 500°C, about 550°C, about 600°C, about 650°C, about 700°C, or about 750°C.

The drying process in step b) as defined above and/ or the heating process of step c) may be undertaken at a constant or variable temperature. When variable temperature is used, the heating or drying temperature is varied during the course of heating or drying.

The heating process in step c) may be undertaken for a period ranging from about 1 hour to about 20 hours such as about one hour, about 2 hours, about 3 hours, about 5 hours, about 10 hours, or about 20 hours.

The above heating process may be in the form of calcining, which comprise heating the dried mixture of step b) in static or continuous flow of air or oxygen or inert gas.

When a catalyst composition comprising at least one promoter is desired, step a) of the method above may be modified accordingly, that is step a) may comprise adding a support to at least one metal precursor and at least one promoter precursor, wherein said at least one metal precursor and at least one promoter precursor are dissolved in a solvent or a mixture of solvents.

The above method for preparing the catalyst composition may be termed as wet impregnation technology.

Exemplary, non-limiting embodiments of a method for converting an alkene to a diene will now be disclosed.

The present disclosure provides a method for converting an alkene to a diene comprising the step of

exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition comprises:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

Further, the present disclosure provides a method for converting an alkene to a diene comprising the step of

exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition consists essentially of:

- a. at least one metal oxide;
- b. optionally a promoter; and
- c. a support.

In an exemplary embodiment, the present disclosure provides a method for converting an alkene to a diene comprising the step of

exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition comprises:

- 5 a. at least one metal oxide;
 b. at least one promoter; and
 c. a support.

In another exemplary embodiment, the present disclosure additionally provides a method for converting an alkene to a diene comprising the step of

- 10 exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition consists essentially of:

- a. at least one metal oxide;
 b. at least one promoter; and
 c. a support.

- 15 The step of converting the alkene to the diene may be undertaken until a substantial deactivation of the catalyst occurs, wherein the substantial deactivation is about 20 to 30% decrease from the initial activity of the catalyst.

- The catalyst composition as defined herein may be regenerated and reused. Prior to a regeneration step, the reaction chamber may be purged with inert gas (which may be nitrogen, argon or helium) followed by charging the oxygen or other suitable gas to the reactor in order to remove the unwanted residues on the catalyst such as coke and at the same time to regenerate the catalyst. Once the catalyst composition is regenerated, inert gas may then be introduced to the reaction chamber to remove the oxygen residue before the regenerated catalyst is used for the next cycle of the reaction.
- 20

- 25 The method for converting the alkene to the diene in the presence of the catalyst composition as defined above may be undertaken under process conditions such as the amount of the at least one metal oxide, a promoter and a support as defined above as well as at the temperature range previously defined.

- The above method may be useful for converting 1-butene to 1,3-butadiene. Thus, the present disclosure also provides a method for preparing 1,3-butadiene from 1-butene comprising the step of
- 30

exposing a reactant stream of the 1-butene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition comprises:

- 35 a. indium oxide (In_2O_3);
 b. Pt and P_2O_5 as promoters; and
 c. Al_2O_3 as catalyst support.

The present disclosure also provides a method for converting 1-butene to 1,3-butadiene comprising the step of

exposing a reactant stream of the 1-butene to a catalyst composition at a temperature of at least 500°C, wherein said catalyst composition consists essentially of:

- a. indium oxide (In_2O_3);
- b. Pt and P_2O_5 as promoters; and
- c. Al_2O_3 as catalyst support.

The method for converting 1-butene to 1,3-butadiene in the presence of the catalyst composition as defined above may be undertaken under process conditions such as the amount of indium oxide, Pt and P_2O_5 as promoters and Al_2O_3 as catalyst support as defined above as well as at the temperature range previously defined.

In summary, it can be deduced that the catalytic oxidative dehydrogenation of 1-butene using the catalyst composition defined herein has potential and is considered attractive thus far as a low-cost starting material such as 1-butene can be extracted from natural gas condensates and refinery waste gases or can be converted from 1-butanol, which production has been improved by virtue of sufficient supply of bioethanol generated from biomass resources.

Further, from the process point of view, oxidative dehydrogenation has advantages compared to other processes such as direct dehydrogenation, mainly due to less energy consumption, higher theoretical conversion and longer catalyst life.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves 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 the limits of the invention.

Fig.1

[Fig. 1] is a number of graphs describing the catalytic performance of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ in Example 2a in terms of 1,3-butadiene (BD) yield, BD selectivity and conversion at different reaction temperatures. Fig. 1(A) illustrates the (BD) yield, BD selectivity and conversion at four different reaction temperatures. Fig. 1(B) depicts the selectivity of the three products i.e. *cis*-2-butene, *trans*-2-butene and 1,3-butadiene (BD). The values of the selectivity for *cis*-2-butene at four different temperatures are 41, 36, 22 and 12, respectively. The values of the selectivity for *trans*-2-butene at four different temperatures are 58, 48, 29 and 15, respectively. The values of the selectivity for 1,3-butadiene (BD) at four different temperatures are 5, 14, 34 and 41, respectively.

Fig.2

[Fig. 2] is a number of graphs describing the catalytic performance of the catalyst composition in Example 2a based on the concentration of In_2O_3 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst at constant temperature of 600°C. Fig. 2(A) depicts the conversion achieved with 0 wt%, 5 wt%, 10 wt%, 25 wt%, 50 wt% of In_2O_3 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Fig. 2(B) shows the 1,3-butadiene (BD) selectivity achieved with 0 wt%, 5 wt%, 10 wt%, 25 wt%, 50 wt% of In_2O_3

in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Fig. 2(C) depicts the BD yield achieved with 0 wt%, 5 wt%, 10 wt%, 25 wt%, 50 wt% of In_2O_3 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.

Fig.3

[Fig. 3] is a number of graphs describing the effect of the concentration of P_2O_5 (as promoter) in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst of Example 2b on the catalytic performance of the catalyst composition at constant temperature of 600°C and constant concentration of In_2O_3 at 25 wt%. Fig. 3(A) depicts the conversion achieved with 0 wt%, 1 wt%, 2 wt%, 3 wt%, 5 wt%, 10 wt%, 15 wt% of P_2O_5 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Fig. 3(B) shows the 1,3-butadiene (BD) selectivity achieved with 0 wt%, 1 wt%, 2 wt%, 3 wt%, 5 wt%, 10 wt%, 15 wt% of P_2O_5 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Fig. 3(C) depicts the BD yield achieved with 0 wt%, 1 wt%, 2 wt%, 3 wt%, 5 wt%, 10 wt%, 15 wt% of P_2O_5 in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.

Fig.4

[Fig. 4] is a histogram to compare the BD yield achieved in the oxidative dehydrogenation of 1-butene performed at two reaction temperatures 550°C and 600°C as described in Example 2b.

Fig.5

[Fig. 5] is a histogram describing the effect of the type of promoter and its concentration on the catalytic performance of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst described in Example 2c. Specifically, this fig. depicts the BD yield achieved with various promoters (La, Pt, Ni, Zn, Ag, P_2O_5 , Ce, Mn or Mo) in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst at three different temperatures 550°C , 600°C and 650°C .

Fig.6

[Fig. 6] is a number of graphs describing the catalytic performance of the catalyst composition comprising P and Pt (as two promoters) in $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst at constant concentration of In_2O_3 of 25 wt% and at reaction temperatures of 500°C , 550°C and 600°C as described in Example 2d. The catalytic performance was evaluated in terms of the BD yield.

Fig.7

[Fig. 7] is a number of graphs showing the catalytic performance of the regenerated catalyst composition at 600°C as described in Example 3. “#” refers to the number of reaction cycle. For clarity, #2 means that the catalyst composition has been used once before and regenerated prior to being subjected to the second reaction cycle. Fig. 7(A) describes the conversion of the regenerated catalyst composition (25 wt% of In_2O_3 , 5 wt% of P_2O_5 and 2 wt% of $\text{Pt}/\text{Al}_2\text{O}_3$). Fig. 7(b) shows the BD selectivity of the regenerated catalyst composition (25 wt% of In_2O_3 , 5 wt% of P_2O_5 and 2 wt% of $\text{Pt}/\text{Al}_2\text{O}_3$). Fig. 7(C) describes the BD yield of the regenerated catalyst composition (25 wt% of In_2O_3 , 5 wt% of P_2O_5 and 2 wt% of $\text{Pt}/\text{Al}_2\text{O}_3$). Fig. 7(D) depicts the BD yield of the regenerated catalyst composition (25 wt% of In_2O_3 , 2 wt% of P_2O_5 and 2 wt% of $\text{Pt}/\text{Al}_2\text{O}_3$).

Examples

Non-limiting examples of the invention and a comparative example 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.

5 **Example 1: Preparation of Al₂O₃ Supported In₂O₃ Catalyst**

a) Al₂O₃ Supported In₂O₃ Catalyst of Different In₂O₃ Loading (Al₂O₃/In₂O₃)

A required amount of In(NO₃)₃·xH₂O (purity 99.9%, purchased from Sigma-Aldrich of St. Louis, Missouri of the United States of America), depending on the desired wt% of In₂O₃, was dissolved in 20 mL deionized (DI) water. The mixture was then transferred into a round bottom flask (RBF). The RBF was rotated at about 100 rpm for about 30 minutes to obtain a homogeneous solution. About 1 gram of solid Al₂O₃ support was then added, and the mixture was stirred at 30 rpm for about 3 hours to achieve uniform immersion.

The uniform mixture was then dried under 72 mbar degassing, 100 rpm rotation and 50°C heating. The Al₂O₃ supported In₂O₃ catalyst was further dried in an oven for about 12 hours at 110°C. Finally, the catalyst was subjected to calcination in static air at 600°C for 3 hours.

b) Al₂O₃ Supported In₂O₃ Catalyst Having Different Phosphorous Loading (P-Al₂O₃/In₂O₃)

A required amount of In(NO₃)₃·xH₂O and concentrated H₃PO₄, depending on the desired wt% of P in the catalyst system, was dissolved in 20 mL deionized (DI) water. The mixture was then transferred into a round bottom flask (RBF). The RBF was rotated at about 100 rpm for about 30 minutes to obtain a homogeneous solution. About 1 gram of solid Al₂O₃ support was then added, and the mixture was further stirred at 30 rpm for about 3 hours to achieve uniform immersion.

The uniform mixture was then dried under 72 mbar degassing, 100 rpm rotation and 50°C heating. The Al₂O₃ supported In₂O₃ catalyst was further dried in an oven for about 12 hours at 110°C. Finally, the catalyst was subjected to calcination in static air at 600°C for 3 hours.

c) P-Al₂O₃/In₂O₃ With Different Pt Loading

A required amount of In(NO₃)₃·xH₂O, concentrated H₃PO₄, and H₂PtCl₆·xH₂O (purity 99.9%, purchased from Sigma-Aldrich of St. Louis, Missouri of the United States of America), depending on the desired wt% of P in the catalyst system, was dissolved in 20 mL deionized (DI) water. The mixture was then transferred into a round bottom flask (RBF). The RBF was rotated at about 100 rpm for about 30 minutes to obtain a homogeneous solution. About 1 gram of solid Al₂O₃ support was then added, and the mixture was further stirred at 30 rpm for about 3 hours to achieve uniform immersion.

The uniform mixture was then dried under 72 mbar degassing, 100 rpm rotation and 50°C heating. The Al₂O₃ supported In₂O₃ catalyst was further dried in an oven for about 12 hours at 110°C. Finally, the catalyst was subjected to calcination in static air at 600°C for about 3 hours.

Example 2: Activity Testing of Al₂O₃ Supported In₂O₃ Catalyst

a) Al₂O₃ Supported In₂O₃ Catalyst of Different In₂O₃ Loading (Al₂O₃/In₂O₃)

The catalytic activity of Al₂O₃/In₂O₃ was evaluated in a fixed-bed continuous flow reactor. About 100 mg of catalyst was loaded into and packed in a quartz tube. The catalyst was first pre-treated with a continuous flow of helium at about 30 mL/min and at 400°C for one hour prior to the actual reaction.

The pre-mixed 1-butene and carbon dioxide with a ratio of 1 to 9 (1-butene : CO₂ = 1:9) was used as reaction gas. The feeding rate of the reactant mixture was maintained at 30 mL/min (Weight hourly space velocity or “WHSV” was set at about 4.5 h⁻¹). To investigate the effect of the reaction temperature on the activity and selectivity of the catalyst composition, the reaction was performed in the above reactor at reaction temperatures of 500°C, 550°C, 600°C and 650°C, respectively. As can be seen from Fig. 1(A), using Al₂O₃/In₂O₃ catalyst with 10 wt% of In₂O₃ in the catalyst system, 1,3-butadiene (BD) yield, conversion as well as the BD selectivity increase with the temperature. The highest BD selectivity (41) was observed at 650°C (refer to Fig. 1(B)).

The results of the experiment performed at 600°C, which include the conversion, 1,3-butadiene (BD) selectivity and BD yield are shown in Fig. 2. As can be seen from Fig. 2(A), in general, the longer the duration of the reaction, the conversion tends to decrease. Significant erosion in the conversion was observed with the 50 wt% of In₂O₃ in the catalyst. On the other hand, based on Fig. 2(B), the 1,3-butadiene (BD) selectivity increases slightly as the duration of the reaction was increased.

With regard to the 1,3-butadiene (BD) yield, it was observed from Fig. 2(C), that in general the yield also decreases with the increased duration of the reaction. The most noticeable decrease in the BD yield is when 50 wt% of In₂O₃ in the catalyst was used. Interestingly, it is also noted that at higher loadings of In₂O₃, a higher BD yield can be achieved. However, the catalyst composition has a short lifetime.

b) Al₂O₃ Supported In₂O₃ Catalyst Having Different Phosphorous Loading (P-Al₂O₃/In₂O₃)

The catalytic activity of P-Al₂O₃/In₂O₃ was evaluated in a similar manner as section a). About 100 mg of catalyst was loaded into and packed in a quartz tube to obtain a fixed-bed reactor system. The catalyst was first pre-treated with a continuous flow of helium at about 30 mL/min and at 400°C for one hour prior to the actual reaction.

The pre-mixed 1-butene and carbon dioxide with a ratio of 1 to 9 (1-butene : CO₂ = 1:9) was used as reaction gas. The feeding rate of the reactant mixture was maintained at 30 mL/min (Weight hourly space velocity or “WHSV” was set at about 4.5 h⁻¹).

The results of the experiment performed at 600°C, which include the conversion, 1,3-butadiene (BD) selectivity and BD yield are shown in Fig. 3. As can be seen from Fig. 3(A), generally, the conversion increases with the increase of the P-loading (up to about 5 wt%). Interestingly, it is noted from Fig. 3(B) that the 1,3-butadiene (BD) selectivity increases with the increase of the P-loading.

With regard to the 1,3-butadiene (BD) yield, as can be seen from Fig. 3(C), that in general the yield increases with the increase of the P-loading. This observation suggests that the presence of phosphorous in the catalyst system can enhance the BD yield.

To further investigate the effect of the reaction temperature on the performance of P-Al₂O₃/In₂O₃ catalyst, an experiment having similar set of reaction conditions, except that the reaction was run at a lower temperature of 550°C, was carried out for each of the following P-loading: 1 wt%, 2 wt%, 3 wt%, 5 wt%, 10 wt%, and 15 wt%. The yield was monitored and compared with that obtained at higher temperature of 600°C. As can be seen from Fig. 4, P-Al₂O₃/In₂O₃ catalyst appears to perform better at a higher temperature of 600°C, in particular for 5 wt% P₂O₅/Al₂O₃.

c) Al₂O₃ Supported In₂O₃ Catalyst With Different Promoters (Promoter-Al₂O₃/In₂O₃)

The catalytic activity of Al₂O₃/In₂O₃ comprising different promoter (including phosphorous) was evaluated in a similar manner as section a). About 100 mg of catalyst was loaded into and packed in a quartz tube to obtain a fixed-bed reactor system. The catalyst was first pre-treated with a continuous flow of helium at about 30 mL/min and at 400°C for one hour prior to the actual reaction.

The pre-mixed 1-butene and carbon dioxide with a ratio of 1 to 9 (1-butene : CO₂ = 1:9) was used as reaction gas. The feeding rate of the reactant mixture was maintained at 30 mL/min (Weight hourly space velocity or “WHSV” was set at about 4.5 h⁻¹).

The results of the experiment performed at 550°C, 600°C and 650°C, which is represented by the 1,3-butadiene (BD) yield are shown in Fig. 5. With reference to this fig, it can be deduced that the BD yield is generally higher when the reaction was performed at 600°C. At this temperature, the highest BD yield was achieved using P or Pt as the promoter. Interestingly, when the reaction duration was extended from 10 minutes to 35 minutes, the BD yield in general decreases, which may be due to the catalyst deactivation.

d) Al₂O₃ Supported In₂O₃ Catalyst Having Two Promoters (P-Pt-Al₂O₃/In₂O₃)

The catalytic activity of Al₂O₃/In₂O₃ having phosphorous and platinum as promoters was assessed in a similar manner as section a). About 100 mg of catalyst was loaded into and packed in a quartz tube to obtain a fixed-bed reactor. The catalyst was first pre-treated with a continuous flow of helium at about 30 mL/min and at 400°C for one hour prior to the actual reaction.

The pre-mixed 1-butene and carbon dioxide at a ratio of 1 to 9 (1-butene : CO₂ = 1:9) was used as reaction gas. The feeding rate of the reactant mixture was maintained at 30 mL/min (Weight hourly space velocity or “WHSV” was set at about 4.5 h⁻¹).

The results of the experiment performed at 550°C, 600°C and 650°C, which is represented by the 1,3-butadiene (BD) yield are depicted in Fig. 6. In this fig, it can be seen that the presence of platinum as promoter appears to enhance the BD yield at 550°C. On the other hand, P appears to be more suitable used as the promoter at 600°C.

Example 3: Regeneration of Al₂O₃ Supported In₂O₃ Catalyst

To evaluate the performance of the regenerated catalyst, the catalytic activity was evaluated in an automatic fixed-bed continuous flow reactor with cyclic program. About 200 mg of the catalyst composition was mixed with 730 mg quartz sands. The mixture was then loaded into
5 and packed in a quartz tube.

The catalyst composition was first pre-treated with a continuous flow of helium at 30 mL/min, at 400°C for one hour. Premixed 1-butene and CO₂ (1-butene : CO₂ = 1 : 9) was used as reaction gas and the feeding rate of this reactant mixture was set at 50 mL/min (WHSV = 4.5 h⁻¹).

The reaction was carried out for 150 minutes at about 600°C. At the end of the reaction, the
10 feeding gas was switched from the reaction gas to helium. The system was then cooled down to 500°C and maintained at this condition for about one hour. Purified air (PA) having a flow rate of 30 mL/min was fed into the reactor for regeneration process at 500°C for approximately one hour.

Finally, the reactor system was subjected to a further cooling under continuous flow of helium
15 to 400°C. At this stage, the catalyst composition was regenerated and ready to be used for next cycle of pre-treatment and reaction. The catalytic performance of the regenerated catalyst compositions i.e. first one being 25 wt% of In₂O₃, 5 wt% of P₂O₅ and 2 wt% of Pt/Al₂O₃ and the second one being 25 wt% of In₂O₃, 2 wt% of P₂O₅ and 2 wt% of Pt/Al₂O₃ at 600°C is depicted in Figs. 7 in terms of conversion, BD selectivity as well as BD yield. Based on Figs. 7(A), 7(B)
20 and 7(C), it can be seen that the catalyst composition can be regenerated and suitably reused up to 40 cycles of reaction without any significant reduction in its performance.

Industrial Applicability

As the catalyst composition as defined herein confers benefits and/ or advantages described above, such catalyst composition may be used for converting short chains of alkene into its
25 corresponding diene in industrial setting.

It is known that 1,3-butadiene (BD) is used primarily in the production of synthetic rubber such as styrene-butadiene rubber (SBR), polybutadiene rubber, and nylon intermediate i.e. adiponitrile. It is also known that a copolymer of styrene and butadiene such as acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene (NBR) and styrene-butadiene (SBR) can
30 be used in automobile tires.

Further, 1,3-butadiene (BD) is also useful in the manufacture of other synthetic rubber materials such as chloroprene, solvent such as sulfolane and the synthesis of cycloalkanes and cycloalkenes. Based on the above, the catalyst composition as defined herein is
35 industrially applicable at least in the processes or manufacture of the chemicals outlined above.

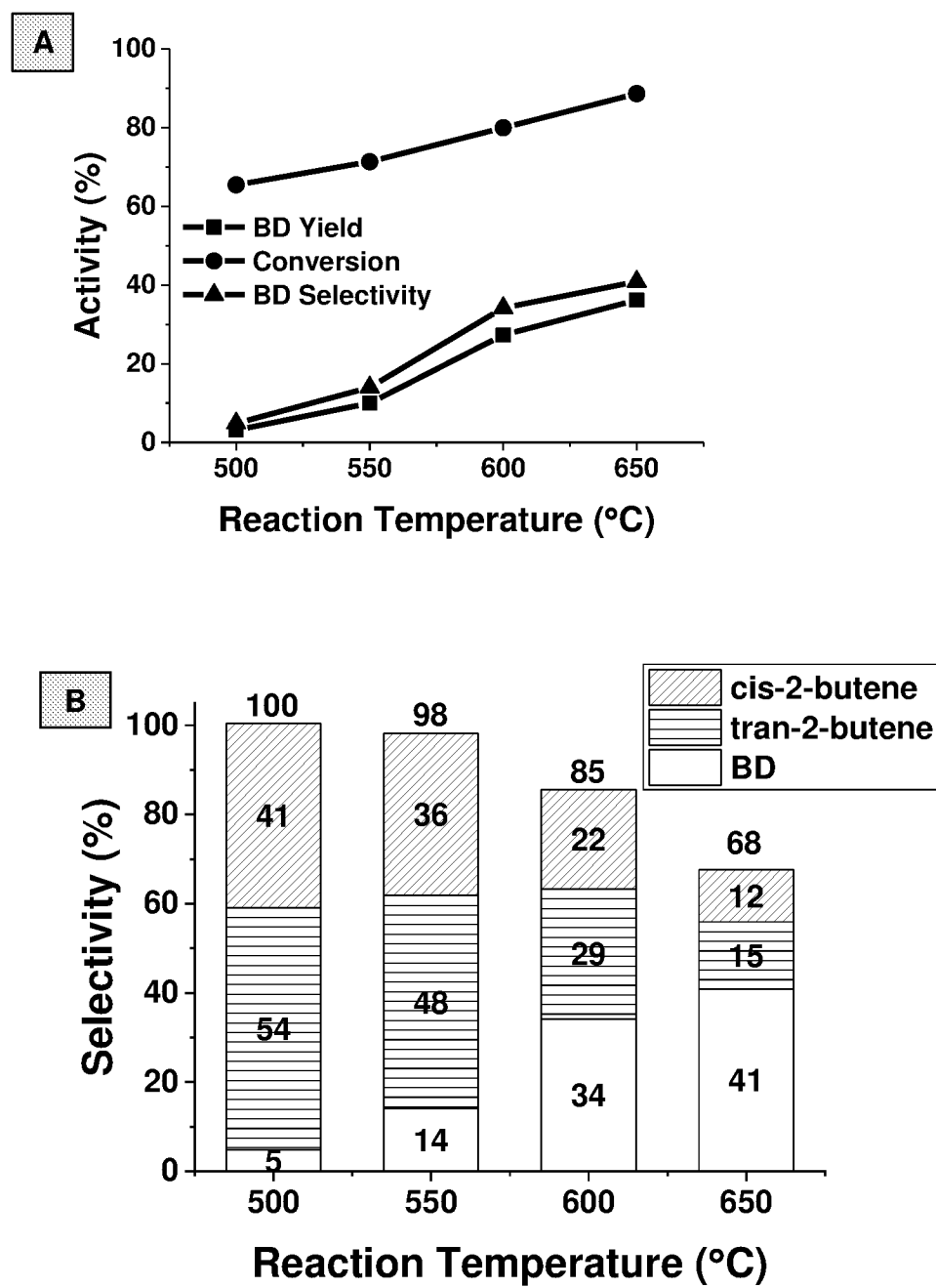
It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come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

Claims

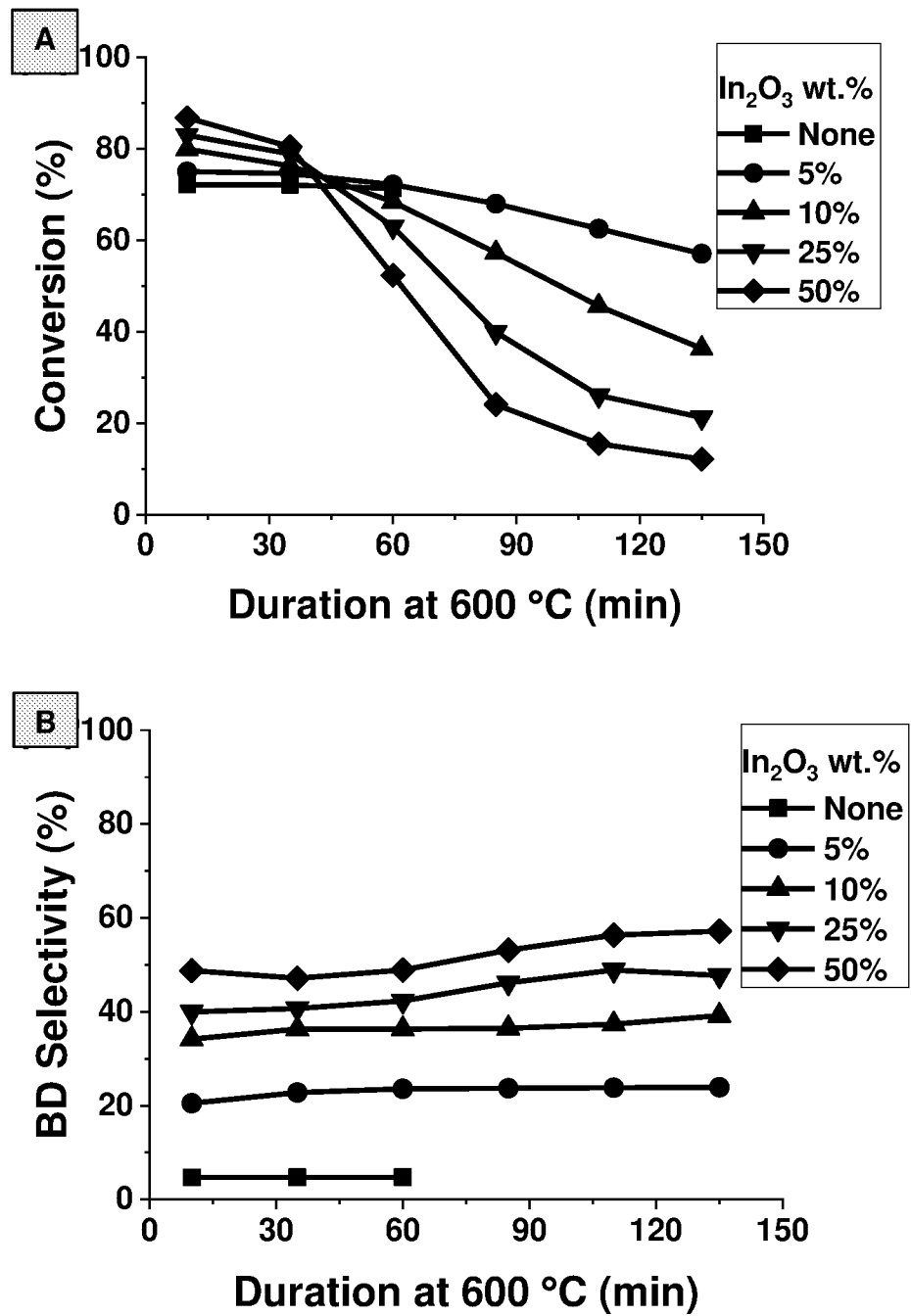
1. A catalyst composition comprising:
 - a) at least one metal oxide;
 - b) optionally a promoter; and
 - 5 c) a support.
2. The catalyst composition according to claim 1, wherein the metal of the at least one metal oxide is a transition metal, a non-transition metal or a combination thereof or an alloy thereof.
3. The catalyst composition according to claim 2, wherein the transition metal is
10 selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), zirconium (Zr) and zinc (Zn).
4. The catalyst composition according to claim 2, wherein the non-transition metal is selected from the group consisting of aluminium (Al), cadmium (Cd), indium (In), tin (Sn), lead (Pb), thallium (Tl) and bismuth (Bi).
- 15 5. The catalyst composition according to any one of claims 1 to 3, wherein the at least one metal oxide is TiO_2 , VO_2 , V_2O_5 , CrO , Cr_2O_3 , MnO , Mn_2O_3 , Mn_3O_4 , Mn_2O_7 , CoO , Co_2O_3 , Co_3O_4 , NiO , Ni_2O_3 , ZrO_2 , ZnO , a combination thereof or an alloy thereof.
6. The catalyst composition according to any one of claims 1, 2 or 4, wherein the at least one metal oxide is Al_2O_3 , CdO , In_2O_3 , SnO_2 and PbO , a combination thereof or an alloy
20 thereof.
7. The catalyst composition according to any one of the preceding claims, wherein the promoter is an oxide of a non-metal element, a transition metal, a non-transition metal or mixtures thereof.
8. The catalyst composition according to claim 7, wherein the oxide of the non-metal
25 element is selected from the group consisting of P_2O_5 , P_4O_6 , As_2O_5 , Sb_4O_6 , SeO_2 , SeO_3 , Bi_2O_3 , TeO_2 , and TeO_3 .
9. The catalyst composition according to claim 7, wherein the transition metal is selected from a transition metal in Group IIIB, IVB, VB, VIB, VIIB, VIII, IB or IIB of the Periodic Table.
- 30 10. The catalyst composition according to claim 7, wherein the non-transition metal is an alkali or alkaline earth metal selected from the group consisting of sodium (Na), potassium (K), calcium (Ca), and barium (Ba).
11. The catalyst composition according to any one of the preceding claims, wherein said catalyst composition further comprises an additional promoter.
- 35 12. The catalyst composition according to claim 11, wherein the promoter is Pt and the additional promoter is P_2O_5 or the promoter is P_2O_5 and additional promoter is Pt.

13. The catalyst composition according to any one of the preceding claims, wherein the at least one metal oxide in the catalyst composition is present in a range of about 5 wt.% to 50 wt.%, based on the total weight of the catalyst composition.
14. The catalyst composition according to any one of the preceding claims, wherein the promoter in the catalyst composition is present in an amount ranging from 0 wt.% to 20 wt.%, based on the total weight of the catalyst composition.
15. A method of preparing a catalyst composition comprising the steps of:
- a) adding a support to at least one metal precursor dissolved in a solvent or a mixture of solvents;
 - b) drying the mixture obtained in step a) at a drying temperature; and
 - c) heating the dried mixture obtained in step b).
16. The method of claim 15, wherein the drying temperature of step b) is in a range from 50°C to 120°C.
17. The method of claim 15 or 16, wherein the heating in step c) is undertaken at a heating temperature ranging from 400°C to 800°C.
18. A process of converting an alkene to a diene comprising the step of
- exposing a reactant stream of the alkene to a catalyst composition at a temperature of at least 500°C;
- wherein said catalyst composition comprises:
- a) at least one metal oxide;
 - b) optionally a promoter; and
 - c) a support.
19. The process according to claim 18, wherein the process is undertaken in the presence of an oxidant that is oxygen or carbon dioxide.
20. The process according to claim 18 or 19, wherein the alkene has 2 to 6 carbon atoms.
21. The process according to any one of claims 18 to 20, wherein the catalyst composition is capable of being regenerated or reused.
22. The process according to any one of claims 18 to 21, wherein said alkene is 1-butene and said diene is 1,3-butadiene.

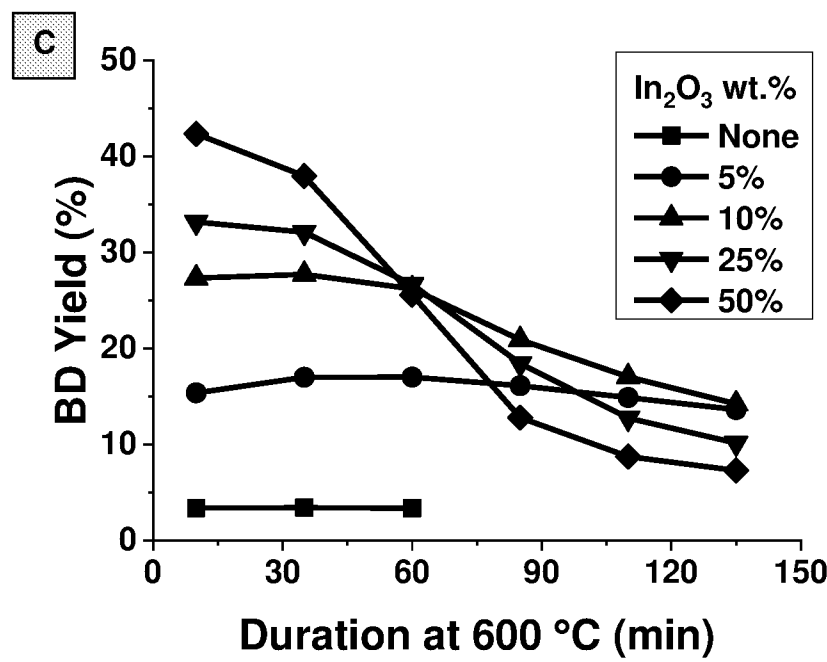
[Fig. 1]



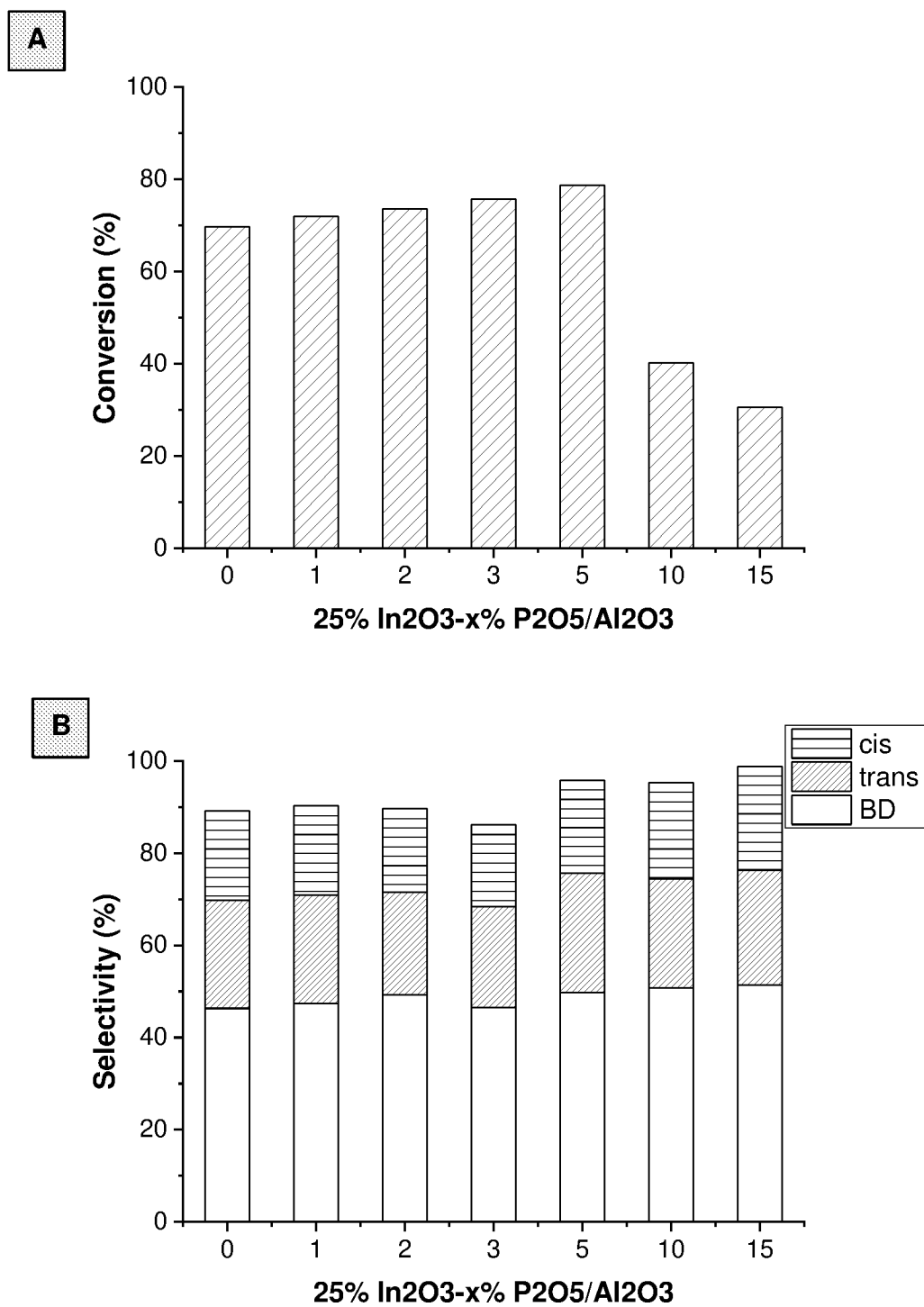
[Fig. 2]



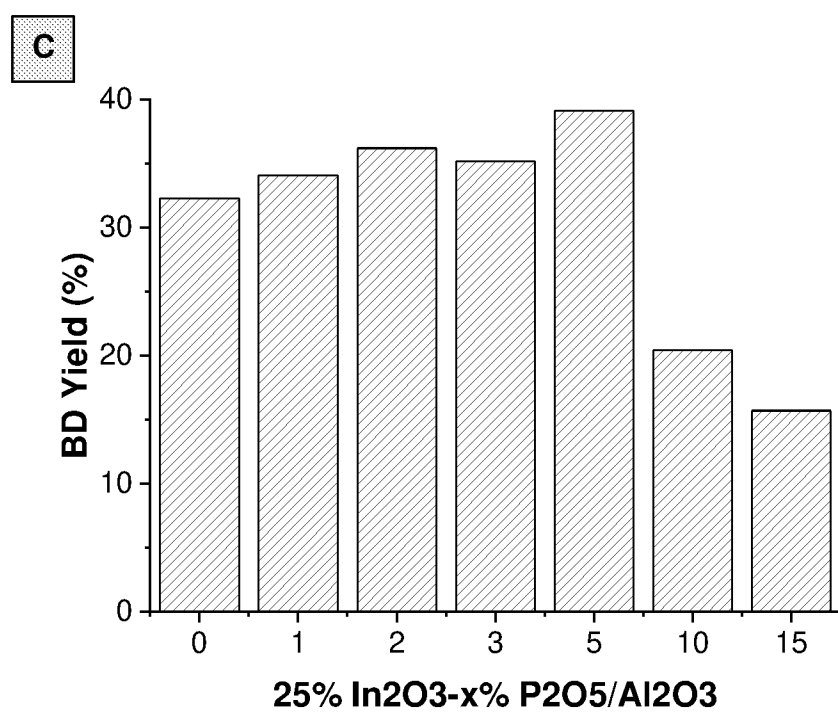
[Fig. 2]



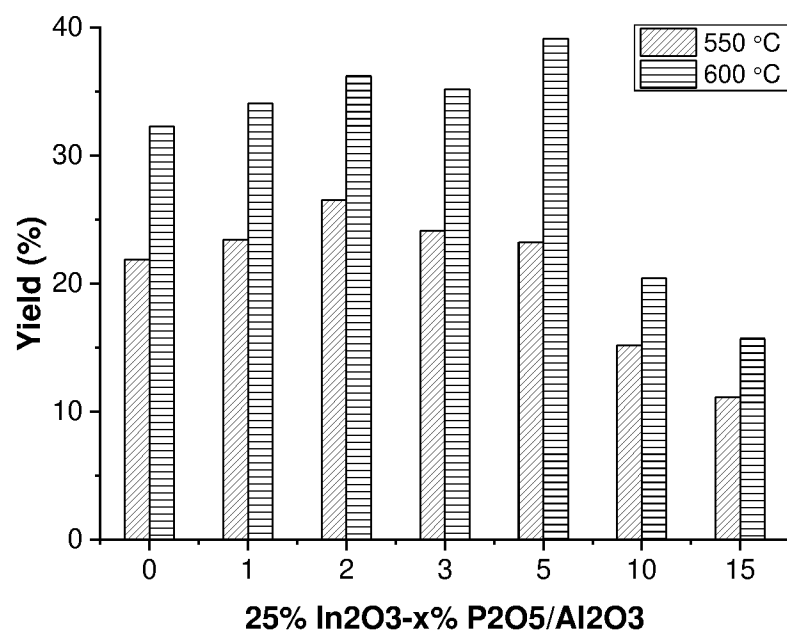
[Fig. 3]



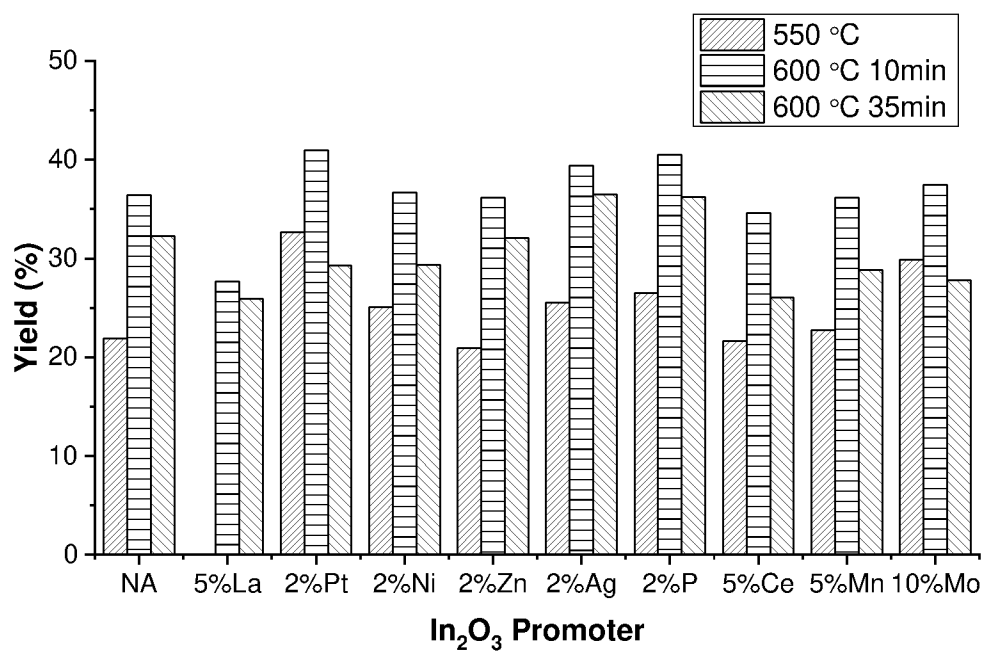
[Fig. 3]



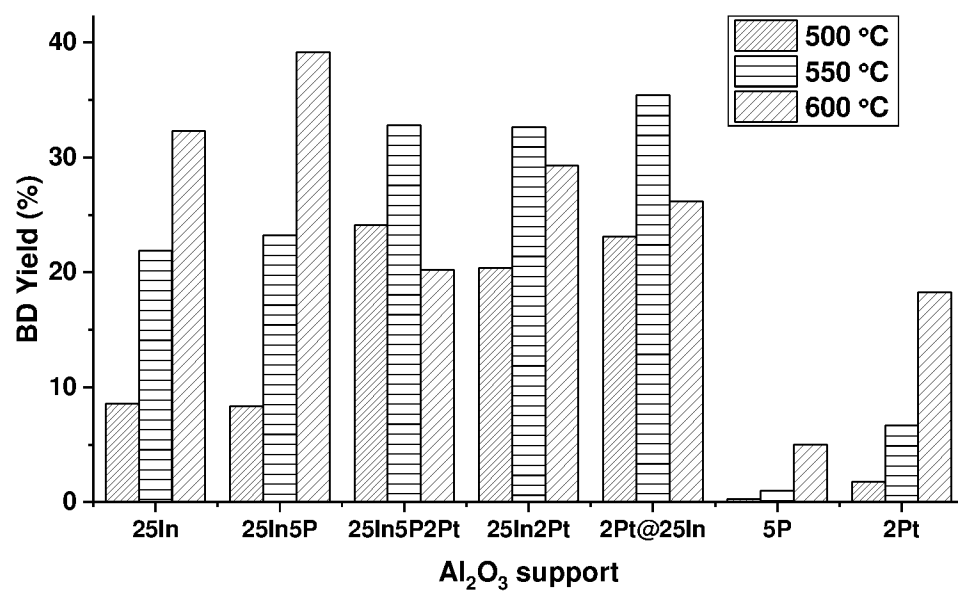
[Fig. 4]



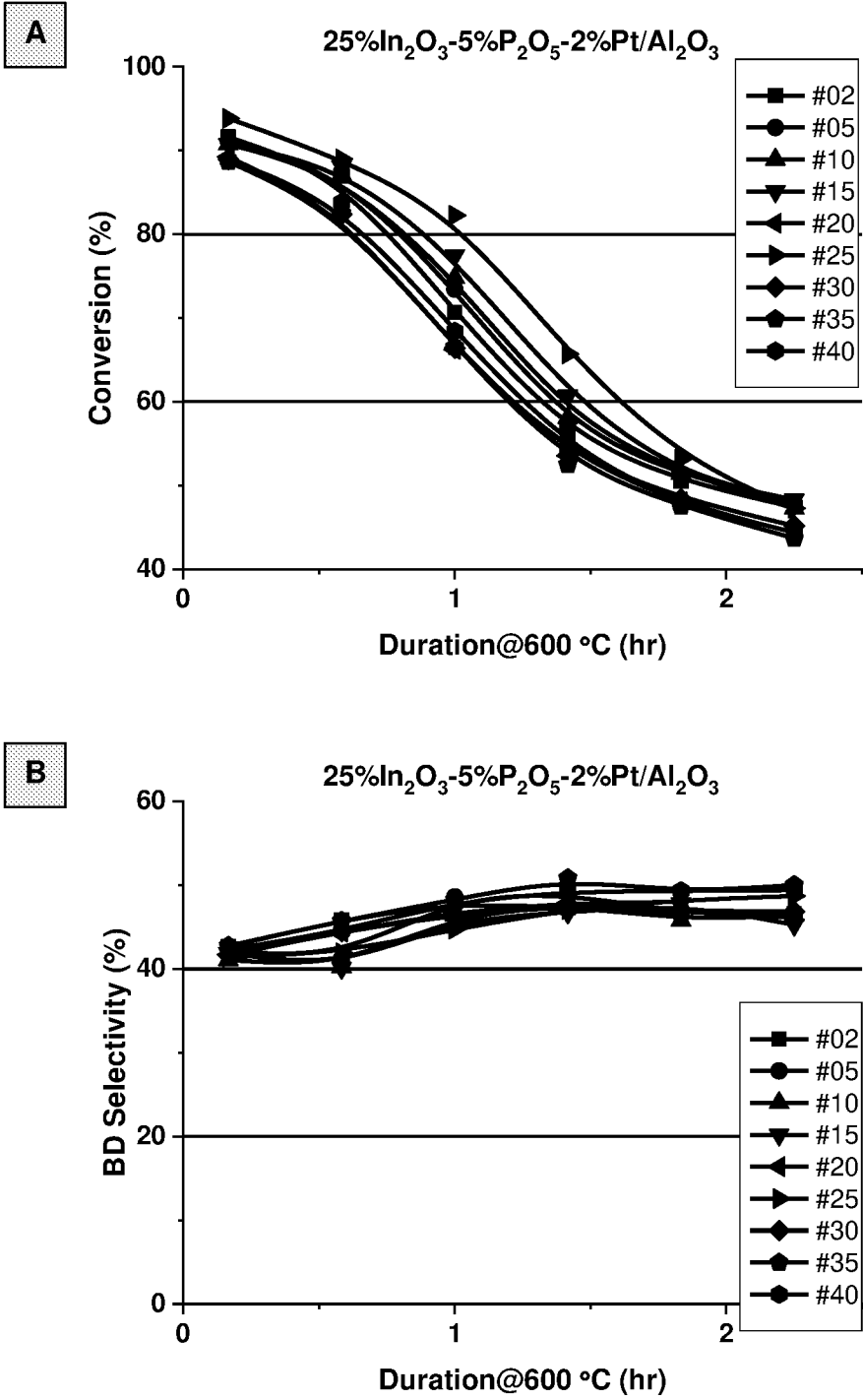
[Fig. 5]



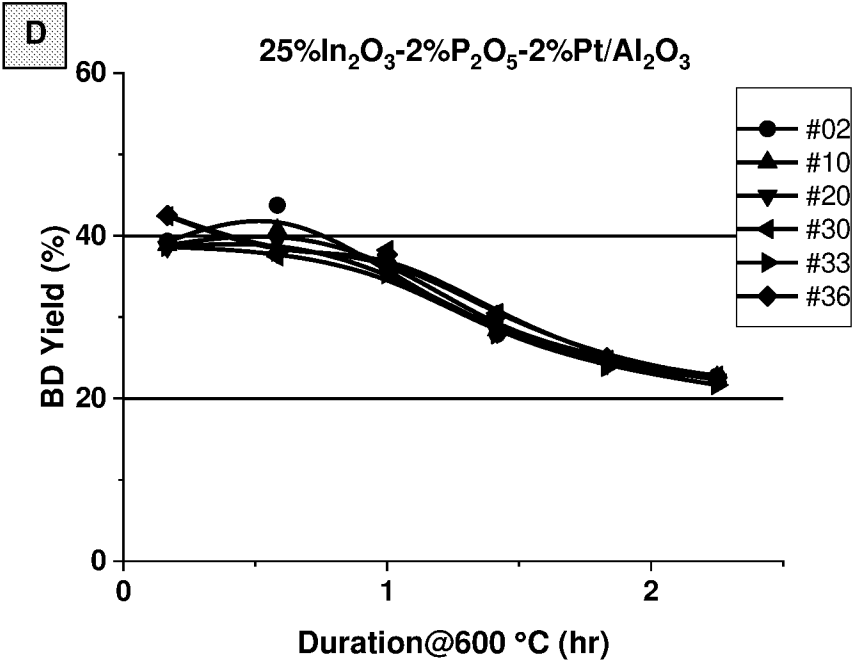
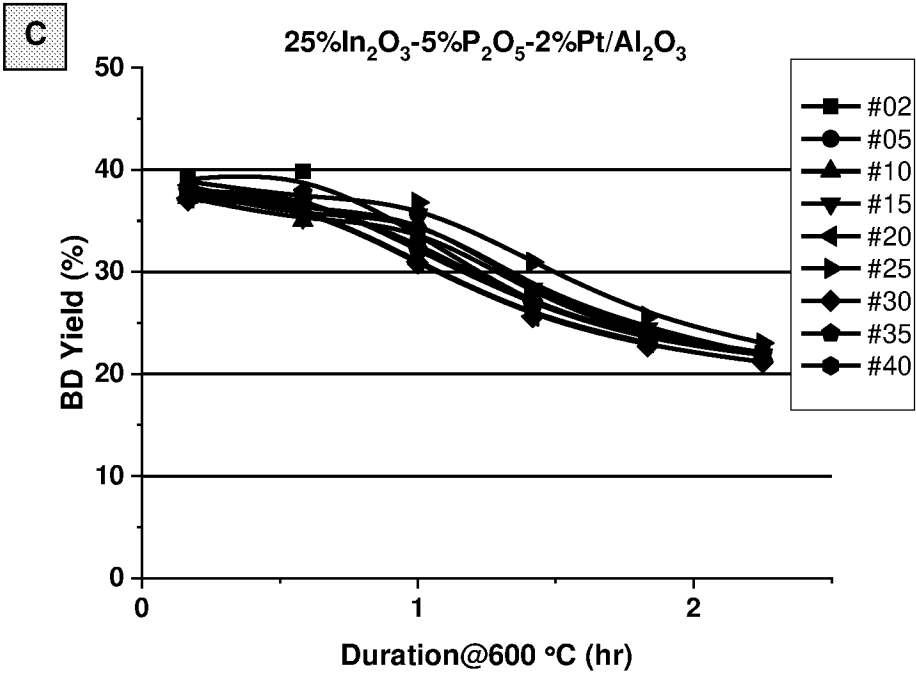
[Fig. 6]



[Fig. 7]



[Fig. 7]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050320

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J, C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: CAPLUS and FAMPAT

Keywords: indium oxide, In_2O_3 , promoter, platinum, phosphorus pentoxide, P_2O_5 , support, carrier, alumina, silica, butene, butadiene, oxidative dehydrogenation, and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GAO, Y. ET AL., Catalytic oxidative dehydrogenation of 1-butene to 1,3-butadiene with CO_2 over $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts: the effect of acid or alkali modification. <i>Reaction Kinetics, Mechanisms and Catalysis</i> , 12 June 2017, Vol. 122, No. 1, pages 451 – 462 [Retrieved on 2019-09-06] <DOI: 10.1007/S11144-017-1205-Z> (see Abstract and Experimental)	1 – 8, 10 – 11 and 13 – 22
X	US 3390202 A (CALLAHAN, J. L. ET AL.) 25 June 1986 (see col. 4 lines 8 – 31, Examples I and IV)	1 – 2 and 7 – 22
X	US 2005/0137083 A1 (ROCHA, T. G. ET AL.) 23 June 2005 (Abstract, [0006], [0027] – [0029] and Catalysts 7 and 8 in Table 1)	1 – 2, 4, 6 – 7, 9, 11 and 13 – 17
X	US 5068480 A (TAKAGAWA, M. ET AL.) 26 November 1991 (see Examples and Table I)	1 – 8, 11 and 13 – 17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

06/09/2019

(day/month/year)

Date of mailing of the international search report

09/09/2019

(day/month/year)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050320

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0155157 A1 (ZARRINPASHNE, S. ET AL.) 13 July 2006 (see [0020], [0035] – [0046] and Catalyst B)	1 – 6, 11 and 13 – 17
X	US 2004/0063578 A1 (MORTON, R. W. ET AL.) 1 April 2004 (see Example III)	1 – 2, 4, 6 – 7, 11 and 13 – 14
X	CN 107537534 A (CHINA PETROLEUM & CHEM CORP ET AL.) 5 January 2018 (see Examples and Table 1) of the machine translation	1 – 8, 11 and 13 – 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050320

Supplemental Box (Classification of Subject Matter)

Int. Cl.

B01J 23/08 (2006.01)

B01J 23/62 (2006.01)

B01J 27/18 (2006.01)

B01J 21/04 (2006.01)

C07C 5/48 (2006.01)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2019/050320

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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CN 107537534 A	05/01/2018	NONE	