HETEROGENEOUS CATALYSTS FOR THE
OXIDATIVE DEHYDROGENATION OF
ALKANES OR OXIDATIVE COUPLING OF
METHANE

Applicant: Wisconsin Alumni Research
Foundation, Madison, WI (US)

Inventors: Ivo Hermans, Middleton, WI (US);
William Peter McDermott, Madison,
WI (US); Joseph Thomas Grant,
Madison, WI (US); Juan Maricio
Venegas, Madison, WI (US);
Somphonh Peter Phivilay,
Madison, WI (US)

Assignee: Wisconsin Alumni Research
Foundation, Madison, WI (US)

Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 138 days.

Appl. No.: 15/643,693
Filed: July 7, 2017

Prior Publication Data

Related U.S. Application Data
Continuation-in-part of application No. 15/260,649,
filed on Sep. 9, 2016.

Int. Cl.
C07C 2/84 (2006.01)
B01J 21/02 (2006.01)
C07C 5/48 (2006.01)
B01J 27/24 (2006.01)

Improved methods of oxidative dehydrogenation (ODH) of
short chain alkanes or ethylene to the corresponding
oligomers, and improved methods of oxidative coupling of
methane (OCM) to ethylene and/or ethane, are disclosed.
The disclosed methods use boron- or nitride-containing
catalysts, and result in improved selectivity and/or byprod-
uct profiles than methods using conventional ODH or OCM
catalysts.

ABSTRACT

17 Claims, 34 Drawing Sheets
(11 of 34 Drawing Sheet(s) Filed in Color)
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Figure 2
Figure 7A
Figure 9

C₃H₈ conversion, C₃H₆ yield (%) vs. Time on stream (hours)

24  20  16  12  8  4  0

Conversion

Yield
Figure 10

$40 \text{mg BNNT}$

$-r_{\text{C}_3\text{H}_8} = 3.5 \times 10^{-2}$

$[\text{mol C}_3\text{H}_8 \text{ kg-cat}^{-1} \text{s}^{-1}]$

$300 \text{mg hBN}$

$-r_{\text{C}_3\text{H}_8} = 1.7 \times 10^{-3}$

$[\text{mol C}_3\text{H}_8 \text{ kg-cat}^{-1} \text{s}^{-1}]$
Figure 11A

[Graph showing data points and curves indicating the relationship between different variables.]
$-r_{CH_4} = k \frac{P_{CH_4}^2}{K_P O_2 + 1}$

Figure 11B
Figure 14

Product selectivity (%) vs. C<sub>3</sub>H<sub>8</sub> conversion (%)

- propene
- CO<sub>2</sub>
- CO
- ethene
- methane

h-BN Sigma-Aldrich batch #1
h-BN Sigma-Aldrich batch #2
h-BN Alfa-Aesar
BNNT, LLC
Figure 20

$T = 490^\circ C$
$P_{\text{case}} = 0.3\text{ atm}$
$P_{\text{O}_2} = 0.15\text{ atm}$

300 mg hBN: $h_{\text{HNO}_3}$
- $f_{\text{C}_3\text{H}_8} = 3.93 \times 10^{-3} \text{ (mol C}_3\text{H}_8\text{ kg-cat}^{-1}\text{s}^{-1})$

300 mg hBN: $f_{\text{C}_3\text{H}_8} = 2.80 \times 10^{-3} \text{ (mol C}_3\text{H}_8\text{ kg-cat}^{-1}\text{s}^{-1})$

WHSV$^{-1}$ (kg-cat s mol C$_3$H$_8^{-1}$)

$\% \text{CH}_3\text{OH}$
Figure 22

- c-B, propylene selectivity
- c-B, olefin selectivity

C<sub>3</sub>H<sub>8</sub> Conversion (%) vs. C<sub>3</sub>H<sub>6</sub> Selectivity (%)
Figure 24
Figure 27

- olefins
- propylene

- c-B
- ac-B
- a-B
- a-B, 94-96% pure, O is major impurity
- a-B, 90% pure, Mg is major impurity
Figure 31

Selectivity (%) vs. n-C₄H₁₀ conversion (%)

- 1-butene
- trans-2-butene
- cis-2-butene
- 1,3-butadiene
- propylene
- ethylene
- CO
- CO₂
- C4 olefins
- olefins
HETEROGENEOUS CATALYSTS FOR THE OXIDATIVE DEHYDROGENATION OF ALKANES OR OXIDATIVE COUPLING OF METHANE

FIELD OF THE INVENTION

C₃ and C₄ olefins, such as propylene (propene), 1-butene, isobutene and butadiene, are widely used starting materials in the industrial synthesis of a variety of important chemical products. The principal industrial method for producing C₃ and C₄ olefins is steam cracking, a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. The products obtained by steam cracking depend on the composition of the feed, the hydrocarbon-to-steam ratio, and on the cracking temperature and furnace residence time. For example, a feed composition that primarily contains ethane (ethane cracking) would result in high ethylene yields, while a feed composition including larger hydrocarbons, such as naphtha (naphtha cracking), would result in a larger yield of C₃ and C₄ olefins.

Over the last decade, the demand for C₃ and C₄ olefins has outstripped supply from traditional cracker units, and this trend is expected to accelerate over the next decade. For example, the current world demand for propene is around 100 million metric tons per year (MTA), and is expected to increase significantly over the next five years. This trend is primarily due to the availability of cheap shale gas, prompting many chemical companies to convert their naphtha crackers into ethylene crackers, thus shifting production towards ethylene and away from longer chain C₂ and C₄ olefins. Accordingly, the demand for C₃ and C₄ olefins is growing faster than can be supplied by only cracking.

Because C₃ and C₄ olefin production by conventional steam cracking has not kept pace with rising demand, several alternative “on-purpose” olefin production technologies have been developed. These technologies include the catalytic dehydrogenation (DH) of short chain alkanes to the corresponding olefins, as well as improved methods for catalyzing the oxidative dehydrogenation of methane to form ethane and/or ethylene. These methods make use of catalysts containing boron, nitride, or both, to substantially increase selectivity (and productivity) for the desired olefin reaction product, while greatly decreasing the production of unwanted byproducts, such as CO and CO₂. As a result, even after more than 30 years of research into catalysis development for ODH (almost entirely focused on supporting vanadium oxide on amorphous oxide supports (e.g., SiO₂, Al₂O₃, TiO₂, CeO₂, ZrO₂) and structured oxides (e.g., MCM-41, SBA-15)), ODH has not been successfully used in the industrial-scale production of C₃ and C₄ olefins.

BRIEF SUMMARY

We disclose herein new and improved methods for catalyzing the oxidative dehydrogenation of C₃-C₄ alkanes or ethylbenzene to the corresponding C₃-C₄ olefins or styrene, as well as improved methods for catalyzing the oxidative coupling of methane to form ethane and/or ethylene. The improved methods use catalysts containing boron, nitride, or both, to substantially increase selectivity (and productivity) for the desired olefin reaction product, while greatly decreasing the production of unwanted byproducts, such as CO and CO₂. In a non-limiting example, use of the disclosed catalyst for ODH of propane to propene (ODHP) provided 77% propene selectivity at 17% propane conversion, with the byproducts being primarily ethylene, and with negligible CO₂ formation. The exemplary catalyst stayed active over 8 days with no need for regeneration treatment, showing a marked improvement in reactivity over this time period.
catalyzed by the heterogeneous catalyst include oxidative dehydrogenation (ODH) or oxidative methane coupling (also known as oxidative coupling of methane, OCM).

In some embodiments, the process catalyzed by the heterogeneous catalyst is not zero order with respect to oxygen.

In some embodiments, the liquid or gaseous reactant is an alkane. In some such embodiments, the alkane is a C₂-C₄ n-alkane or isoo-alkane. In some such embodiments, the alkane is a C₃-C₅ alkane, including without limitation a C₃-C₅ n-alkane or iso-alkane. In some such embodiments, the C₃-C₅ alkane is propane, n-butane, or isobutane, and the one or more desired chemical products may include propene, isobutene, 1-butene, 2-butene, and/or butadiene.

In some embodiments, the oxygen and one or more liquid or gaseous reactants include elemental boron with oxygen and one or more liquid or gaseous reactants. The heterogeneous catalyst catalyzes the oxidative dehydrogenation (ODH) of the one or more liquid or gaseous reactants to form the one or more desired chemical products. In some embodiments, the one or more liquid or gaseous reactants include methane, the heterogeneous catalyst catalyzes the oxidative dehydrogenation (ODH) or oxidative methane coupling (OCM) to form the one or more desired chemical products. In some embodiments, the one or more liquid or gaseous reactants include methane, the heterogeneous catalyst catalyzes oxidative dehydrogenation, and the one or more desired chemical products are olefins. In some such embodiments, the method maintains a greater than 70% selectivity for the desired chemical products (e.g., olefins) at 10% to 20% conversion of the alkane. In some such embodiments, the method maintains a greater than 77% selectivity for the olefin at 10% to 20% conversion of the alkane. In some such embodiments, the method maintains a greater than 80% selectivity for the olefin at 10% to 20% conversion of the alkane.

In some embodiments, the method maintains a greater than 70% selectivity for the desired chemical products (e.g., olefins) at 10% to 20% conversion of the alkane. In some such embodiments, the alkane is n-butane and the desired chemical products include 1-butene and/or 2-butene. In some embodiments, the alkane is isobutane and the desired chemical products include isobutene.

In some embodiments, the one or more liquid or gaseous reactants include ethylene. In some such embodiments, the method exhibits a 90% selectivity for the olefin at 10% to 20% conversion of the alkane. In some such embodiments, the one or more liquid or gaseous reactants include an alkane or a hydrocarbon comprising an alkyl group. In some such embodiments, the one or more liquid or gaseous reactants include methane, the heterogeneous catalyst catalyzes the oxidative dehydrogenation of the one or more liquid or gaseous reactants. The heterogeneous catalyst catalyzes the oxidative dehydrogenation (ODH) of the one or more liquid or gaseous reactants or the oxidative coupling of methane (OCM) to form the one or more desired chemical products. In some embodiments, the one or more liquid or gaseous reactants include an alkane. Non-limiting examples include C₃-C₄ n-alkanes or C₃-C₄ iso-alkanes. In some such embodiments, the alkane is a C₂-C₄ n-alkane or a C₂-C₄ iso-alkane. In some such embodiments, the one or more liquid or gaseous reactants include ethylene, propane, n-butane, or isobutane, and the corresponding one or more desired chemical products may be ethene, propene, isobutene, 1-butene, 2-butene or butadiene. In some such embodiments, the C₂-C₄ n-alkane is propane and the desired chemical products are olefins. In some such embodiments, the one or more liquid or gaseous reactants include ethylene, the heterogeneous catalyst catalyzes the oxidative coupling of methane, and the one or more

80 m² g⁻¹, greater than 90 m² g⁻¹, greater than 100 m² g⁻¹, greater than 110 m² g⁻¹, greater than 120 m² g⁻¹, greater than 130 m² g⁻¹, greater than 140 m² g⁻¹, greater than 150 m² g⁻¹, greater than 180 m² g⁻¹, greater than 200 m² g⁻¹, greater than 250 m² g⁻¹, greater than 300 m² g⁻¹, greater than 350 m³ g⁻¹, greater than 400 m³ g⁻¹, greater than 450 m³ g⁻¹, or greater than 500 m³ g⁻¹. In some such embodiments, the boron nitride has a surface area of about 20 m² g⁻¹ to 550 m² g⁻¹, about 9 m² g⁻¹ to 550 m² g⁻¹, about 50 m² g⁻¹ to 550 m² g⁻¹, about 100 m² g⁻¹ to 500 m² g⁻¹, or about 100 m² g⁻¹ to 200 m² g⁻¹. In certain exemplary embodiments, the boron nitride has a surface area of about 150 m² g⁻¹, about 180 m² g⁻¹, about 200 m² g⁻¹, about 250 m² g⁻¹, about 300 m² g⁻¹, about 350 m² g⁻¹, about 450 m² g⁻¹, or about 500 m² g⁻¹.
desired chemical products include ethane and/or ethylene. In some such embodiments, the heterogeneous catalyst is contacted with natural gas.

In some embodiments, the elemental boron is in the form of crystalline boron (c-B), amorphous boron (a-B), or a mixture of amorphous and crystalline boron (ac-B).

In some embodiments, the heterogeneous catalyst is made up of at least 90% elemental boron or at least 98% elemental boron by weight.

In some embodiments, the heterogeneous catalyst consists essentially of elemental boron.

In some embodiments, the heterogeneous catalyst further includes magnesium, oxygen, or both magnesium and oxygen.

In some embodiments, the Brunauer-Emmett-Teller (BET) surface area of the heterogeneous catalyst is from 0.50 to 550 m² g⁻¹. In some such embodiments, the heterogeneous catalyst has a surface area range of 0.70 m² g⁻¹ to 500 m² g⁻¹, 0.80 m² g⁻¹ to 200 m² g⁻¹, 0.90 m² g⁻¹ to 100 m² g⁻¹, or 1.0 m² g⁻¹ to 20 m² g⁻¹.

In some embodiments, the average particle size of the heterogeneous catalyst is from 0.20 to 1.5 µm.

In some embodiments, the contacting step occurs at a temperature of from 400° C. to 900° C.

In some embodiments, the oxygen and one or more liquid or gaseous reactants are in a reactant stream that is contacted with the heterogeneous catalyst. In some such embodiments, the reactant stream includes from 0% to 70% nitrogen by weight.

Further objects, features and advantages of the invention will be apparent from the following detailed description when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing selectivity to propene plotted against propane conversion for ODHP using boron nitride (BN) and conventional catalysts. The BN catalyst shows much more stable propene selectivity with increasing propane conversion than the more traditional vanadium oxide catalyst supported on SiO₂ (V/SiO₂) or SBA-15 (V/SBA-15).

FIG. 2 is a graph showing the relationship between product selectivities and propane conversion percentages when using vanadium oxide supported on SiO₂ (V/SiO₂) or the BN catalyst. Product selectivities are represented by the bar plots and are shown on the left-axis, while propane conversions are represented by the black diamonds and are shown on the right-axis.

FIG. 3 is a graph showing the results of a long-term stability test completed using the BN catalyst to look for any indication of catalyst deactivation. Propane conversion and propene yield (filled-black square and open-black square, respectively) are shown on the left-axis, while propene selectivity (circle) is shown on the right-axis.

FIG. 4 is a graph showing high propene selectivity at relatively high propane conversions with the use of the BN catalyst, confirmed from BN provided by two separate chemical suppliers.

FIG. 5 is a graph showing product selectivities and propane conversion percentages using various boron- or nitride-containing catalysts that were screened for oxidative dehydrogenation of propane (ODHP). Product selectivities are represented by the bar plots and are shown on the left-axis, while propane conversion percentages are represented by the black diamonds and are shown on the right-axis.

FIG. 6 is a graph showing selectivity to propene plotted against propane conversion for ODHP using a variety of catalysts. Both boron- and nitride-containing catalysts show activity for ODHP.


FIG. 7B is a bar graph showing comparisons of ODHP product selectivity among V/SiO₂ (X₃CH₃=5.8%), h-BN (X₃CH₃=5.4%) and BNNT (X₃CH₃=6.5%) catalysts. Product selectivity is represented by shaded bars. Gas contact times (WHHSV⁻¹) were varied to achieve a range of conversions and differ depending on the reactivity of the material; V/SiO₂: 5-15 kg-cat s mol C₃H₈⁻¹; h-BN: 15-40; BNNT: 2-5; T=490° C., P₀₂=0.15 atm, P₃CH₃=0.3 atm.

FIG. 7C is a graph showing comparisons of ODHP propane productivity (kg-C₃H₈ kg-cat⁻¹ h⁻¹) plotted as a function of C₃H₈ conversion among V/SiO₂, h-BN, and BNNT catalysts. The great selectivity to propane afforded by BN materials, coupled with the increased activity of BNNT, leads to superior productivity using BNNT. Gas contact times (WHHSV⁻¹) were varied to achieve a range of conversions and differ depending on the reactivity of the material; V/SiO₂: 5-15 kg-cat s mol C₃H₈⁻¹; h-BN: 15-40; BNNT: 2-5; T=490° C., P₀₂=0.15 atm, P₃CH₃=0.3 atm.

FIG. 8 is a graph showing ODHP selectivity to olefins (propene+ethene) (filled shapes), as well as oxygen conversion (open shapes), plotted against propane conversion, comparing hexagonal boron nitride (h-BN, square shapes) and boron nitride nanotubes (BNNT, circular shapes). Use of BN materials results in higher olefin selectivity and lower consecutive propene over-oxidation (corresponding to the slope of these curves) than when using V/SiO₂. Oxygen remains present even at high propane conversion. Gas contact time with these catalysts varies depending on the
reactivity of the material; h-BN: 15-40 (kg-cat s mol C₃H₈⁻¹); V/SiO₂: 5-15 (kg-cat s mol C₃H₈⁻¹); BNNT: 2-5 (kg-cat s mol C₃H₈⁻¹); T=490° C., P₂O₅=0.15 atm, P_C₃H₈=0.3 atm (balance N₂).

FIG. 9 is a graph showing ODHP propane conversion and propene yield as a function of time on stream using h-BN. Propane conversion (diamonds, right-axis) and product selectivity (bars, left-axis) using untreated h-BN (hBN) and oxygen functionalized h-BN (hBN_HNO₃) as ODHP catalysts. BN materials show much higher selectivity to olefins than the traditional V/SiO₂ catalyst, which shows high selectivity to COX (40%), WHSV⁻¹: 16-48 (kg-cat s mol C₃H₈⁻¹) [V/SiO₂]; 44-111 (kg-cat s mol C₃H₈⁻¹) [h-BN]; 4-12 (kg-cat s mol C₃H₈⁻¹) [BNNT]; T=440° C., P₂O₅=0.1 atm, P_C₄H₁₀=0.1 atm (balance N₂).

FIG. 10 is a graph showing ODHP propane conversion plotted as a function of inverse-weight-hour-space-velocity (WHSV⁻¹), kg-cat s mol C₃H₈⁻¹, comparing h-BN (lower right line) to BNNT (upper left line) catalysts. The slope of each of these lines indicates the rate of propane consumption. Much less BNNT is needed to achieve equivalent conversions when using h-BN as a consequence of the superior reactivity of the BNNT material. T=490° C., WHSV⁻¹:24 kg-cat s mol C₃H₈⁻¹, P₂O₅=0.2 atm, P_C₃H₈=0.3 atm (balance N₂).

FIG. 11A and 11B are graphs showing rates of ODHP propane consumption using h-BN as a function of (11A) P₂O₅ (P_C₃H₈ constant at 0.3 atm), and (B) P_C₃H₈ (P₂O₅ constant at 0.2 atm) fit with Eley-Rideal kinetics, showing O₂ adsorption and second-order dependence with respect to P_C₃H₈. Solid lines are a least-square fit taking into account all experimental data points at each temperature using the rate law displayed in FIG. 11B. FIG. 12 is a bar graph showing metal impurity analysis of BN materials from various suppliers (Sigma-Aldrich, Alfa-Aesar, and BNNT, LLC), as well as two batches from Sigma-Aldrich (batch #1: Lot STBF0279V; batch #2: Lot STBF7843V). Additional metals (Ni, Pt, V, Cu, Zr, Ga, Mo, Ag, and Na) were screened, but always registered below the detection limit.

FIG. 13 is a graph showing ODHP propane selectivity plotted as a function of propane conversion for h-BN supplied by Alfa-Aesar and Sigma-Aldrich (batch #1: Lot STBF0279V; circles; batch #2: Lot STBF7843V, triangles) and BNNT (BNNT, LLC, diamonds). Despite slight differences in metal impurities between batches and suppliers, selectivity to propene between samples is almost identical (±5%). WHSV⁻¹: 15-40 (kg-cat s mol C₃H₈⁻¹) [h-BN]; 2-5 (kg-cat s mol C₃H₈⁻¹) [BNNT]; T=490° C., P₂O₅=0.15 atm, P_C₃H₈=0.3 atm (balance N₂).

FIG. 14 is a bar graph showing comparisons of ODHP propane conversion (diamonds, right-axis) and product selectivity (bars, left-axis) among different BN suppliers (Sigma-Aldrich, Alfa-Aesar, and BNNT, LLC) and batches of h-BN from Sigma-Aldrich (batch #1: Lot STBF0279V; batch #2: Lot STBF7843V). Despite slight differences in metal impurities between batches and supplier, product selectivity between samples are almost identical. WHSV⁻¹: 15-40 (kg-cat s mol C₃H₈⁻¹) [h-BN]; 2-5 (kg-cat s mol C₃H₈⁻¹) [BNNT]; T=490° C., P₂O₅=0.15 atm, P_C₃H₈=0.3 atm (balance N₂).

FIG. 15 is a graph showing that both boron- and nitride-containing catalysts, including nickel boride (Ni-boride) show activity for oxidative dehydrogenation of propane (ODHP); T=490° C., P₂O₅=0.15 atm, P_C₃H₈=0.3 atm. FIG. 16 is a graph showing BN nanotube n-butane ODHP conversion (black squares, right axis) and product selectivity (bars, left axis) as a function of reaction temperature. C₄ selectivity combines selectivity to 1-butene and 2-butenes. FIG. 17 is a graph comparing BN nanotube n-butane ODHP conversion (x-axis) and C₄ selectivity (y-axis) with reported state of the art catalysts, p-CNT denotes functionalized carbon nanotubes. BNNTs show comparable selectivity to the most selective catalysts reported. Open symbols indicate reactivity data from other works, cited within the FIG. 1-3; 1: Zhang, J.; Liu, X.; Blume, R.; Zhang, A.; Schlogl, R.; Su, D. S. Science. 2008, 322 (5989), 73-77.; 2: Nieto, J. M. T.; Conception, P.; Dejer, a.; Knozinger, H.; Melo, F.; Vazquez, M. J. J. Catal. 2000, 189 (1), 147-157; 3: Madeira, L. M.; Portela, M. F. Catal. Rev. 2002, 44 (2), 247-286.)

FIG. 18 is a graph showing comparisons of isobutane conversion (diamonds, right-axis) and product selectivity (bars, left-axis) when using vanadium oxide supported on silica (V/SiO₂), hexagonal BN (h-BN), and BN nanotubes (BNNT) as catalysts for ODH of isobutane. BN materials show much higher selectivity to olefins than the traditional V/SiO₂ catalyst, which shows high selectivity to COX (40%), WHSV⁻¹: 16-48 (kg-cat s mol C₄H₁₀⁻¹) [V/SiO₂]; 44-111 (kg-cat s mol C₄H₁₀⁻¹) [h-BN]; 4-12 (kg-cat s mol C₄H₁₀⁻¹) [BNNT]; T=440° C., P₂O₅=0.1 atm, P_C₄H₁₀=0.1 atm (balance N₂).

FIG. 19 is a graph showing product selectivity (y-axis) plotted against isobutane conversion (x-axis) when using vanadium oxide supported on silica (V/SiO₂), hexagonal BN (h-BN), and BN nanotubes (BNNT) as catalysts for ODH of isobutane. WHSV⁻¹: 16-48 (kg-cat s mol C₄H₁₀⁻¹) [V/SiO₂]; 44-111 (kg-cat s mol C₄H₁₀⁻¹) [h-BN]; 4-12 (kg-cat s mol C₄H₁₀⁻¹) [BNNT]; T=440° C., P₂O₅=0.1 atm, P_C₄H₁₀=0.1 atm (balance N₂).

FIG. 20 is a graph showing propane consumption when using untreated h-BN (hBN) and oxygen functionalized h-BN (hBN_HNO₃) as ODHP catalysts. Oxygen functionalized h-BN shows ~40% higher rate of propane consumption as compared to untreated h-BN.

FIG. 21 is a graph showing selectivity to propene plotted against propane conversion for the ODH of propane using several catalysts, including crystalline boron (42.0 mg c-B with QC, 77.5 mg c-B without QC, 300.0 mg c-B without QC), boron nitride nanotubes (BNNTs), and hexagonal boron nitride (h-BN). The results illustrate that crystalline elemental boron catalyzes ODHP. T=490° C.; P_C₄H₁₀=0.30 atm; P₂O₅=0.15 atm; P_N₂=0.55 atm; flow (F)=40-170 mL min⁻¹.

FIG. 22 is a graph showing selectivity to both propene (lower dotted line, solid circles) and all olefins (upper line, open circles) plotted against propane conversion for the ODH of propane using crystalline boron (c-B) as the catalyst. The difference between olefin selectivity and the selectivity specifically to propene is accounted for by ethylene production, while the difference between olefin selectivity and 100% selectivity is accounted for by the production of CO, CO₂, and methane side products. The results illustrate that ethylene is the major side product of c-B catalyzed ODHP. T=490° C.; P_C₄H₁₀=0.30 atm; P₂O₅=0.15 atm; P_N₂=0.55 atm; flow (F)=40-170 mL min⁻¹.

FIG. 23 is a bar graph showing product distribution comparisons (ODHP propane conversion shown by solid squares, plotted to right-axis; product selectivity for propylene, CO₂, CO, ethylene, methane, and C₄s shown by bars, plotted to left-axis) using crystalline boron (c-B), hexagonal boron nitride (h-BN), and boron nitride nanotube (BNNTs) as catalysts. Product distribution profiles are similar for the three catalysts. T=490° C.; P_C₄H₁₀=0.30 atm; P₂O₅=0.15 atm; P_N₂=0.55 atm.

FIG. 24 is a graph showing selectivity to propene plotted against propane conversion for the ODH of propane using several catalysts, including crystalline boron (c-B), a mixture of both crystalline and non-crystalline (amorphous)
Dehydrogenation of propane and isobutane using amorphous and crystalline boron catalysts.

**Results**

- Elemental boron catalyzes the dehydrogenation of propane and isobutane.
- The reaction rate is significantly faster with boron catalysts compared to h-BN.
- The selectivity for propylene and isobutene is substantially higher with boron catalysts.

**Conclusion**

- The use of boron catalysts for dehydrogenation reactions is promising due to their higher productivity and selectivity.

**Detailed Description**

I. In General

Before the present materials and methods are described, it is understood that this invention is not limited to the particular methodology, protocols, materials, and reagents described, as these may vary. It is also to be understood that the terminology used in this disclosure is for the purpose of describing particular embodiments only, and is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.
The following abbreviations are used throughout this disclosure: BN, boron nitride; BN nanomesh(es); boron nitride nanomesh(es); BNNs(s), boron nitride nanosheet(s), BNNS(s), boron nitride nanoribbon(s); BNNR(s), boron nitride nanotube(s); OH, dehydrogenation; h-BN, hexagonal form of boron nitride; OCM, oxidative coupling of methane; ODH, oxidative dehydrogenation; ODHP, oxidative dehydrogenation of propene; P, partial pressure for a given gas; S, selectivity for a given product; WHSV,\(^{-1}\) weight-hour-space-velocity; % X, conversion for a given reactant.

All publications and patents specifically mentioned in this disclosure are incorporated by reference for all purposes, including for describing and disclosing the chemicals, instruments, statistical analysis and methodologies that are reported in the publications that might be used in connection with the disclosed methods and devices. All references cited in this disclosure are to be taken as indicative of the level of skill in the art.

II. The Invention

This disclosure is based on our discovery that the use of a boron- or nitride-containing catalyst facilitates improved oxidative dehydrogenation of alkenes, such as propane, to desired olefins, such as propene. Specifically, the disclosed methods exhibit increased selectivity towards the desired product while decreasing the production of unwanted byproducts, such as CO and CO\(_2\). Furthermore, the process occurs at relatively low temperatures, and the catalyst is stable over time, and so does not need to be frequently regenerated. The catalysts can also be used for oxidative coupling of methane to produce ethane and/or ethylene.

Exemplary Forms of Boron Nitride

Boron nitride (BN) is a non-limiting example of a boron- or nitride-containing catalyst that can be used in the disclosed methods. The boron nitride catalyst can be made from any available form of boron nitride, including, without limitation, amorphous boron nitride (a-BN), hexagonal boron nitride (h-BN), cubic boron nitride (c-BN), wurtzite boron nitride (w-BN), boron nitride-containing composites, boron nitride nanotubes (BNNTs), boron nitride nanosheets (BNNSs), boron nitride nanoribbons (BNNRs) and boron nitride nanomeshes.

h-BN, a stable crystal form of BN, has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces.

As shown in more detail in the examples below, we have determined that the catalytic activity of BN may be enhanced by increasing the surface area of the BN. Accordingly, forms of BN exhibiting increased surface area, such as boron nitride nanotubes and boron nitride nanomeshes, are suitable for use in the disclosed methods.

Boron nitride nanotube(s) (BNNs(s)) are cylindrical structures formed from “rolled up” sheets of alternating and covalently bonded nitrogen and boron atoms. Typical BNNTs have a diameter of several to hundreds of nanometers and a length of many micrometers. They are structurally similar to carbon nanotubes, which self-assemble to form a highly regular mesh. The structure of BN nanomeshes is similar to the structure of graphene, in that they form an assembly of hexagonal pores. In a non-limiting example, the distance between two pores centers is 3.2 nm and the pore diameter is 2 nm, and the pores are about 0.05 nm deep. Other terms used in the literature for this form of boron nitride include h-BN monolayers, boron nitrene, white graphene, boron nitride nanosheets, boron nitride nanoribbons, and boron nitride nanopolymers.

For more information regarding BNNTs and BN nanosheets, see, e.g., A. Colegrove, Y. Bando, Y. Huang, T. Tenero, M. Mitome, C. Tang and C. Zhi, ACS Nano, 4 (6), 2979-2993 (2010).

Oxygen Functionalization of the BN Surface

As shown in more detail in the examples below, we have determined that the catalytic activity of BN may be enhanced by functionalizing the BN surface with oxygen.

The specific method used to functionalize the BN surface with oxygen is not limited, and may include any of a number of methods known in the art. For example, see, D. Jiao et al., (2015) report using silver nanoparticles to oxidize h-BN, with the duration and temperatures used in the procedure affecting the atomic percentage of oxygen functionalized onto the BN surface. Many other methods are known in the art, including the nitric acid treatment used in Example 9 below.

Compositions Containing Elemental Boron

As illustrated in non-limiting Examples 12-14 below, compositions containing elemental boron can be used as catalysts in the disclosed methods. Surprisingly, the use of elemental boron may result in substantially increased productivity, as compared to the use of other boron or nitride-containing catalysts.

The elemental boron-containing compositions include any available form of elemental boron, including, without limitation, amorphous boron (a-B), crystalline boron (c-B), or mixtures of amorphous and crystalline boron (a/c-B). In certain embodiments exhibiting productivity greater than any previously reported catalyst, the elemental boron used is a mixture of amorphous and crystalline boron.

The elemental boron-containing compositions may be substantially pure. For example, the compositions may be made up of 97.0, 97.1, 97.2, 97.3, 97.4, 97.5, 97.6, 97.7, 97.8, 97.9, 98.0, 98.1, 98.2, 98.3, 98.4, 98.5, 98.6, 98.7, 98.8, 98.9, 99.0, 99.1, 99.2, 99.3, 99.4, 99.5, 99.6, 99.7, 99.8, 99.9, or 100.0% boron by weight. Alternately, the compositions may fall within a range of purities that includes any of these percentages except for 100.0% boron as a lower boundary, and any of these percentages except for 97.0% boron as an upper boundary.

Alternatively, the elemental boron-containing compositions may contain a significant percentage of non-boron impurities. For example, the compositions may be made up of 90.0, 90.1, 90.2, 90.3, 90.4, 90.5, 90.6, 90.7, 90.8, 90.9, 91.0, 91.1, 91.2, 91.3, 91.4, 91.5, 91.6, 91.7, 91.8, 91.9, 92.0, 92.1, 92.2, 92.3, 92.4, 92.5, 92.6, 92.7, 92.8, 92.9, 93.0, 93.1, 93.2, 93.3, 93.4, 93.5, 93.6, 93.7, 93.8, 93.9, 94.0, 94.1, 94.2, 94.3, 94.4, 94.5, 94.6, 94.7, 94.8, 94.9, 95.0, 95.1, 95.2, 95.3, 95.4, 95.5, 95.6, 95.7, 95.8, 95.9, 96.0, 96.1, 96.2, 96.3, 96.4, 96.5, 96.6, 96.7, 96.8, 96.9, or 97.0% boron by weight.

Alternately, the compositions may fall within a range of purities that includes any of these percentages except for 97.0% boron as a lower boundary, and any of these percentages except for 90.0% boron as an upper boundary.

In some embodiments, the compositions may fall within a range of purities that includes any of the percentages listed in the previous two paragraphs except for 100.0% boron as a lower boundary, and any of these percentages except for 90.0% B as an upper boundary.
In some embodiments where the compositions contain a significant amount of non-boron impurities, the primary impurities may include oxygen, magnesium, or both oxygen and magnesium.

The elemental boron-containing compositions may have a wide range of Brunauer, Emmett-Teller (BET) surface areas. In some embodiments, the BET surface area is within the range of 0.50 to 550 m$^2$ g$^{-1}$. As non-limiting examples, the BET surface area of the compositions may fall within a range that includes one of 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 5.0, 9.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 50.0, 100.0, 150.0, 200.0, 250.0, 300.0, 350.0, 400.0, 450.0, 500.0, or 550.0 M$^2$ g$^{-1}$ as an upper boundary, and one of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 5.0, 9.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 50.0, 100.0, 150.0, 200.0, 250.0, 300.0, 350.0, 400.0, 450.0, or 500.0 m$^2$ g$^{-1}$ as a lower boundary.

The elemental boron-containing compositions may include a wide range of average particle sizes. In some embodiments, the average particle size is within the range of 0.20 to 1.5 µm. As non-limiting examples, the average particle size of the compositions may fall within a range that includes one of 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4 or 1.5 µm as an upper boundary, and one of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, or 1.4 µm as a lower boundary.

The following examples are offered for illustrative purposes only, and are not intended to limit the scope of the invention in any way. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description and the following Examples and fall within the scope of the appended claims.

III. Examples

Example 1: Substantially Improved Product Selectivity for Oxidative Dehydrogenation of Propane to Propene Using the BN Catalyst

In this example, we demonstrate that using a boron nitride catalyst substantially improves the selectivity of oxidative dehydrogenation of propane to propene (ODHP), particularly at higher conversions, as compared to using conventional ODHP catalysts.

Comprehensive ODHP Results Using Traditional Catalysts and Boron Nitride

ODHP was performed on a gas mixture containing propane (C$_3$H$_8$), Oxygen (O$_2$) and nitrogen (N$_2$) flowing past the BN catalyst made up of boron nitride, a vanadium oxide catalyst supported on SiO$_2$ (V/SiO$_2$), or a vanadium oxide catalyst supported on SBA-15 (V/SBA-15). Operating conditions for both the BN and supported vanadium oxide catalysts were as follows: P$_{O2}$=0.15 atm, P$_{C3H8}$=0.3 atm, P$_{N2}$=0.55 atm, T=490° C. For BN, 200 mg of BN particles 600-710 µm in size were loaded in a 9 mm inner diameter quartz reactor with total inlet flow rates of 40-120 mL min$^{-1}$, equivalent to inverse weight-space-velocity (WHSV$^{-1}$) in the range of 100-300 kg-cat s m$^{-3}$. For V/SiO$_2$, 130 mg V/SiO$_2$ particles 600-710 µm in size (along with 260 mg SiC inert diluent, equivalent in size) were loaded in a 9 mm inner diameter quartz reactor with total inlet flow rates of 60-140 mL min$^{-1}$, equivalent to WHSV$^{-1}$ in the range of 55-130 kg-cat s m$^{-3}$. All carbon balances close to within ±5%. For each catalyst, inlet flows of the C$_3$H$_8$/O$_2$/N$_2$ gas mixture were varied to achieve a range of propane conversions.

Propene selectivity, S, is calculated as follows:

$$S = \frac{F_{\text{C3H6,out}}}{\sum F_{\text{carbon prod}}}$$

where $F_{\text{C3H6,out}}$=flow of propene out of reactor (mol s$^{-1}$ g-cat$^{-1}$)

$F_{\text{carbon prod}}$=flow of all carbon products out of reactor (mol s$^{-1}$ g-cat$^{-1}$)

Propane conversion, X, is calculated as follows:

$$X = \frac{\sum F_{\text{carbon prod}}}{F_{\text{C3H6,in}}}$$

where $F_{\text{C3H6,in}}$=flow of propane into the reactor (mol s$^{-1}$ g-cat$^{-1}$)

Inverse weight-hour-space-velocity, WHSV$^{-1}$ (kg-cat s m$^{-3}$), is calculated as follows:

$$\text{WHSV}^{-1} = \frac{M_{\text{cat}}}{F_{\text{in}}} + 601$$

where $M_{\text{cat}}$=mass of catalyst loaded in reactor (mg)

$F_{\text{in}}$=total flow of all inlet gasses (mL min$^{-1}$)

As seen in FIG. 1, use of the BN catalyst results in a much more stable propene selectivity with increasing propane conversion than the more traditional vanadium oxide catalyst supported on SiO$_2$ or SBA-15. Specifically, BN maintained 77% propene selectivity with 17% propane conversion, while even with a modest 13% propane conversion, the vanadium oxide catalyst supported on SBA-15 shows propene selectivity of 48%.

As seen in FIG. 2, use of the V/SiO$_2$ catalyst (diluted with inert SiC) results in a large drop in propene selectivity with only an increase of ~3% in propane conversion. In contrast, the BN catalyst shows a much more gradual drop in propene selectivity with increasing propane conversion, always showing greater selectivity to propene than the V/SiO$_2$ catalyst, even at ~17% propane conversion.

We further quantify the specific ODHP byproduct results from using the V/SiO$_2$+SiC and BN catalysts, and the results are shown in FIG. 2. When using the BN catalyst, the main byproduct is ethylene, an important chemical building block itself. In contrast, when using the V/SiO$_2$ catalyst, the primary byproducts are CO and CO$_2$. This indicates that BN catalyzes a drastically different mechanism of propene formation than V/SiO$_2$.

In sum, this example demonstrates that improved selectivities and byproduct mix can be obtained by using boron nitride to catalyze ODHP of short chain alkanes to the corresponding olefin, in place of traditional vanadium oxide or other known catalysts.

Example 2: The BN Catalyst is Stable Over the Long Term

A long term stability test was completed using the BN catalyst to look for any indication of catalyst deactivation, and the results are reported in FIG. 3. Operating conditions were as follows: P$_{O2}$=0.3 atm, P$_{C3H8}$=0.3 atm, P$_{N2}$=0.4 atm, T=490° C. All carbon balances close to within ±5%. Testing proceeded for 8.0 day on stream time period.
Referring to FIG. 3, propane conversion and propene yield are shown as a function of time on stream, and the WHSV during various on stream time periods is indicated. After 1.5 days on stream, propane conversion began to increase, along with the natural decrease in propene selectivity, indicating that the BN catalyst was becoming more active. This was likely due to the formation of additional active sites. Total inlet flowrates were then increased from 40 to 50 mL min⁻¹ after 4 days on stream to decrease WHSV⁻¹ from 294 to 234 kg-cat s m⁻³, in order to bring the propane conversion back to its initial value.  After an additional day, total flow rate was again increased (56 mL min⁻¹) to drop WHSV⁻¹ to 210 kg-cat s m⁻³. Propane conversion again increased after several more days, suggesting the continual generation of additional active sites. These results demonstrate that the BN catalyst is stable when used continuously for oxidative dehydrogenation over extended periods of time. Accordingly, the disclosed method is suitable for cost-efficient industrial-scale use.

Example 3: ODHP Catalyzed by Boron Nitride from Multiple Sources Demonstrates Improved Propene Selectivity, with Greater BN Surface Area Facilitating Higher Conversion Rates

In this example, we demonstrate that boron nitride from two different sources catalyzed ODHP with improved selectivity for propene at relatively high conversions. Further analysis revealed that reactivity of BN for ODHP may be proportional to the surface area of the BN catalyst.

Operating conditions were as follows: $P_{\text{O}_2}=0.15$ atm, $P_{\text{C}_3\text{H}_8}=0.3$ atm, $P_{\text{N}_2}=0.55$ atm, $T=490^\circ\text{C}$. 200 mg of BN particles 600-710 µm in size were loaded in a 9 mm ID quartz reactor with total inlet flow rates of 40-120 mL min⁻¹, equivalent to WHSV⁻¹ of 100-300 kg-cat s m⁻³. All carbon balances close to within ±2%. Inlet flow rate of the C₃H₈/O₂/N₂ gas mixture were varied to achieve a range of propane conversions.

BN was used from two separate chemical suppliers: Sigma Aldrich and Alfa Aesar. As seen in FIG. 4, the results were assayed separately, and compared to the results obtained using V/SiO₂. Interestingly, when using identical total inlet flow rates (40 mL min⁻¹), equivalent to 300 kg-cat s m⁻³, the BN supplied from Sigma Aldrich achieved ~17% propane conversion, while the BN supplied from Alfa Aesar only reached 10% propane conversion. This is an indication that the BN from Sigma Aldrich is more reactive per unit of mass than that supplied by Alfa Aesar.

Analysis of the surface area of these two materials (BET) revealed that the Sigma Aldrich BN had a 1.8 times greater specific surface area than the Alfa Aesar BN. Accordingly, the reactivity of BN for oxidative propane dehydrogenation may be proportional to the BN surface area, and therefore could be improved with the synthesis of higher surface area BN materials.

Example 4: Other Boron- or Nitride-Containing Compounds are Active Catalysts for ODHP, with Boron-Containing Compounds Facilitating High Propene Selectivity and Improved Byproduct Mix

In this example, we extended the ODHP catalyst assay disclosed in the previous examples using BN to a range of additional boron- and nitride-containing compounds. The results show that, in general, like BN, boron- and nitride-containing compounds can catalyze ODHP (and likely related ODH of short chain alkanes to corresponding olefins). Furthermore, the results show that in general, like BN, boron-containing compounds catalyze ODHP (and also related ODH of short chain alkanes to corresponding olefins) with greatly improved selectivity for propene and improved byproduct mix.

Various boron- or nitride-containing catalysts were screened for oxidative propane dehydrogenation (ODHP), including B-nitride, Si-nitride, Ti-nitride, Al-nitride, B-carbide, Ti-boride, and Nb-boride. FIG. 5 shows product selectivities of the screened catalysts as a function of propane conversion, and also includes the corresponding data for the conventional V/SiO₂ catalyst. Operating conditions were as follows: $P_{\text{O}_2}=0.15$ atm, $P_{\text{C}_3\text{H}_8}=0.3$ atm, $P_{\text{N}_2}=0.55$ atm, $T=490^\circ\text{C}$. Due to differences in the reactivity between catalysts, total inlet flow rates between catalysts fluctuated between 40 and 140 mL min⁻¹, in order to achieve ~5% propane conversion. About 200 mg of boron- or nitride-containing catalysts 600-710 µm in size were loaded in a 9 mm inner diameter quartz reactor. All carbon balances close to within ±2%.

As seen in FIG. 5, all the tested boron- or nitride-containing catalysts show activity for ODHP. Furthermore, all the tested boron-containing catalysts (B-nitride, B-carbide, Ti-boride, Nb-boride) display high selectivity to propene, with the primary byproduct being ethylene. In contrast, nitride-containing catalysts other than BN (Si-, Ti, Al-nitride) show markedly lower selectivity to propene than the boron-containing alternatives, and produce CO₂ and CO as the primary byproducts.

Inlet flow rates of the C₃H₈/O₂/N₂ gas mixture past the screened boron-containing, nitride-containing and V/SiO₂ catalysts were then varied to achieve a range of propane conversions. Operating conditions were as follows: $P_{\text{O}_2}=0.15$ atm, $P_{\text{C}_3\text{H}_8}=0.3$ atm, $P_{\text{N}_2}=0.55$ atm, $T=490^\circ\text{C}$. About 200 mg of boron- or nitride-containing catalysts 600-710 µm in size were loaded in a 9 mm inner diameter quartz reactor with total inlet flow rates of 40-140 mL min⁻¹, equivalent to WHSV⁻¹ of 100-300 kg-cat s m⁻³. All carbon balances close to within ±5%.

As shown in FIG. 6, the boron-containing catalysts maintained high propene selectivity even at high propane conversions. Nitride-containing catalysts showed lower selectivity to propene, but in the case of Si- and Ti-nitride, propene selectivity did not decrease with increasing propane conversion.

In sum, this example demonstrates that a variety of boron- and nitride-containing catalyst can be used to catalyze the oxidative dehydrogenation of short chain alkanes to corresponding olefins. Furthermore, the results show that in general, like BN, boron-containing compounds catalyze ODHP (and likely related ODH of short chain alkanes to corresponding olefins) with greatly improved selectivity for propene and improved byproduct mix.

In this example, we extend the BN ODH catalyst results disclosed in the previous examples in several specific ways, while providing additional details. First, we demonstrate that effective ODH catalysts can be made from either of two different forms of boron nitride: hexagonal boron nitride (h-BN) or boron nitride nanotubes (BNNTs). BNNT catalysts promote increased propene productivity as compared to h-BN catalysts. Second, we propose a mechanism of action that is consistent with our data that is fundamentally different from the mechanism of action for ODH using traditional catalysts, such as supported vanadia.
Summary.

The exothermic reaction of propane with oxygen to generate propene and water has the potential to be a game-changing technology in the chemical industry. However, even after decades of research, the selectivity to propene remains too low to make the reaction economically attractive. This notoriously low selectivity is due to a fundamental scientific challenge: the desired olefin is much more reactive than the alkane substrate, and is therefore readily oxidized to thermodynamically favored CO₂.

In this example we report that hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) have unique catalytic properties and facilitate an unprecedented selectivity to propene. As an example, at 14% propane conversion, we obtain a selectivity of 77% towards propene and 13% towards ethene, another desired alkene. Based on catalytic experiments, in conjunction with spectroscopic investigations and ab initio modeling, we put forward a mechanistic hypothesis in which oxygen-terminated armchair BN edges are proposed to be the catalytic active sites.

Experiments, Results, and Discussion.

Here, we present both hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) as metal-free materials able to catalyze the ODHP reaction. While graphene and fullerene materials are emerging as catalysts for partial alkane oxidations (D. R. Dreyer, H. P. Jia, C. W. Bielawski, Angew. Chem., 122, 6965-6968 (2010); J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlogl, D. S. Su, Science, 322, 73-77 (2008); B. Frank, J. Zhang, R. Blume, R. Schlogl, D. S. Su, Angew. Chem. Int. Ed., 48, 6913-6917 (2009)), BN materials, one of the “inorganic analogues” of graphene, have yet to be explored in the art for their own catalytic activity. It is actually remarkable that BN, a material deemed to be very stable and inert, is catalytically active at all.

A supported vanadia on silica catalyst (V/SiO₂) was used in this work to make direct comparisons to the catalytic performance of BN. These materials were loaded into a quartz tube reactor heated to 460-500°C under flowing propane, oxygen and nitrogen as an inert carrier gas. Reaction parameters such as temperature, catalyst mass, total gas flow-rate, and partial pressures of propane (PC₃H₈) and oxygen (PO₂) were varied to observe changes to product distributions by sampling the reactor exhaust stream via online gas chromatography and mass spectrometry. Gas contact time with the catalyst is represented in this work as the inverse-weight-hour-space-velocity (WHSV⁻¹, [kg-catalyst parameters such as temperature, catalyst mass, total gas flow-rate, and partial pressures of propane (PC₃H₈) and oxygen (PO₂) were varied to observe changes to product distributions by sampling the reactor exhaust stream via online gas chromatography and mass spectrometry. Gas contact time with the catalyst is represented in this work as the inverse-weight-hour-space-velocity (WHSV⁻¹, [kg-catalyst s mol C₃H₈⁻¹]), which was varied primarily by altering the total gas flow-rate. Use of BN materials results in extraordinary selectivity to propene not observed before under ODHP conditions. For instance, h-BN afforded 77% selectivity to propene at 14% propane conversion (FIG. 7A). Meanwhile, the traditional V/SiO₂ allows for a modest 61% propane selectivity at only 9% propane conversion (J. T. Grant, C. A. Carrero, A. M. Love, R. Verel, I. Hermans, ACS Catal., 5, 5787-5793 (2015)). The obtained selectivities using state-of-the-art ODHP catalysts (1-7; 1: B. Frank, A. Dinse, O. Ovstzer, E. V. Kondratenko, R. Schomaecker, Appl. Catal. A: Gen., 323, 66-76 (2007); 2: C. L. Pieck, M. A. Banares, J. L. G. Fierro, J. Catal., 224, 1-7 (2004); 3: A. Christodoulakis, M. Machli, A. A. Lemonidou, S. Boghosian, J. Catal., 222, 293-301 (2004); 4: P. Viparelli, P. Ciambelli, L. Lisi, G. Ruoppolo, G. Russo, J. C. Volta, Appl. Catal. A: Gen., 184, 291-301 (1999); 5: C. Carrero, M. Kaiser, A. Dinse, T. Wolfram, N. Hamilton, A. Trunschke, R. Schlogl, R. Schomaecker, Catal. Sci. Technol., 4, 786-794 (2014); 6: E. V. Kondratenko, M. Cherian, M. Baerns, D. Su, R. Schlogl, X. Wang, I. E. Wachs, J. Catal., 234, 131-142 (2005); 7: B. Frank, J. Zhang, R. Blume, R. Schlogl, D. S. Su, Angew. Chem. Int. Ed., 48, 6913-6917 (2009))) are compared in FIG. 7A. The decrease in propene selectivity with increasing propane conversion is indicative of the facile over-oxidation of propane to CO₂.

The entire product distribution further distinguishes boron nitride materials from supported vanadia catalysts (FIG. 7B). When using the supported vanadia catalyst the main byproducts are COₓ, accounting for 33% of total product selectivity at 9% propane conversion. Conversely, when using BN materials, the main byproduct is ethene, a highly valuable olefin itself, rather than COₓ. The combined propene and ethene selectivity is 90% at 14% propane conversion using h-BN (FIG. 8). We furthermore verified that the catalytic activity of the BN material remains stable for at least 32 hours on stream (FIG. 9), validating the catalyst stability.

The analogous product distributions for both h-BN and BNNTs suggest a similar reaction mechanism for these BN materials. However, BNNTs exhibit a rate of propane consumption [mol C₃H₈ kg-cat⁻¹ s⁻¹] more than one order-of-magnitude higher than observed with h-BN (FIG. 10). The higher activity of BNNTs at least partially reflects the higher surface area of BNNTs relative to h-BN (BNNT: 97±5 m² g⁻¹ versus h-BN: 16±1 m² g⁻¹) (J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, Nat. Mater., 11, 963-969 (2012)); however, the rate of propane consumption is more than three times higher with BNNT than with h-BN when normalized for surface area (BNNT: 3.6×10⁻¹ mol C₃H₈ s⁻¹ m⁻² versus h-BN: 1.1×10⁻² mol C₃H₈ s⁻¹ m⁻²). This high reactivity and selectivity with BNNTs results in a substantial enhancement in the observed propene productivity [kg-C₃H₆ kg-cat⁻¹ hr⁻¹] (FIG. 7C), comparable to values deemed attractive for commercial implementation of this “on-purpose” propene technology (C. Carrero, M. Kaiser, A. Dinse, T. Wolfram, N. Hamilton, A. Trunschke, R. Schlogl, R. Schomaecker, Catal. Sci. Technol., 4, 786-794 (2014); F. Cavani, N. Ballarini, A. Ceriolo, Catal. Today, 127, 113-131 (2007)).

Further kinetic insights were obtained by studying the influence of reactant concentrations (P₀₂, P₃H₈) on the reaction rate. The inclusion of oxygen as a reactant is required for propane conversion using BN materials. The rate of propane consumption using h-BN indicates oxygen activation on the BN surface (FIG. 11A) and second-order dependence with respect to P₀₂, and first order in propane (K. Chen, A. Khodakov, J. Yang, A. T. Bell, E. Iglesia, J. Catal., 186, 325-333 (1999)).

interesting observations in this example (i.e. improved selectivity to olefins and different reaction kinetics) points towards a novel, fundamentally different reaction mechanism compared to other, well-studied catalysts. Metal impurities in the material are unlikely to play a significant role. Indeed, various boron nitride samples from various suppliers, containing different impurities (FIG. 12) show almost identical catalytic performance (FIGS. 13-14).

Based on semiconductor literature focusing on oxygen-terminated armchair edges of BN (A. L. Bezanilla, J. Huang, H. Terrones, B. G. Sumpter, J. Phys. Chem. C, 116, 15675-15681 (2012)), as well as the proposed active sites of graphene and fullerene materials for other oxidations (J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, D. S. Su, Science, 322, 73-77 (2008); B. Frank, J. Zhang, R. Blume, R. Schlögl, D. S. Su, Angew. Chem. Int. Ed., 48, 6913-6917 (2009)), we propose an oxygen-terminated armchair edge of BN (B—O—O—N<) as the active site for the ODHP reaction. In line with the observed oxygen-dependence of the kinetics, we propose that an oxygen molecule bonded to one B and one N atom acts as the active site. These B—O—O—N< sites can be viewed as inorganic peroxide species, able to perform oxidation reactions.

The second order rate dependence with respect to $F_{\text{C}_{3}\text{H}_{8}}$ suggests that two propane molecules are required to generate two molecules of water, in line with the overall stoichiometry of the reaction. The desorption of water molecules forms BN edge vacancies allowing for unique O$_2$ activation, explaining the influence that the surface coverage of adsorbed oxygen has on the rate of propane consumption.

In summary, this example identifies boron nitride, typically assumed to be inert, as a hitherto unexplored oxidation catalyst. Exceptional selectivity towards propene was obtained during the oxidative dehydrogenation of propane.

Materials and Methods

Hexagonal boron nitride (h-BN, Sigma-Aldrich & Alfa-Aesar) and boron nitride nanotubes (BNNT, BNNT, LLC) were used as provided without further chemical or thermal treatment. Multiple h-BN batches and suppliers were used to ensure reproducibility, and to confirm that it is truly the BN material responsible for catalysis, rather than a potential metal impurity. All suppliers guarantee >99% purity of h-BN and BNNT, which is confirmed with our own metal impurity analysis using induced coupled plasma optical emission spectroscopy (ICP-OES) (FIG. 12).

Acid digestion of BN materials was completed by refluxing ~10 mg BN in 6 mL aqua regia solution (3:1 HCl: HNO3) overnight, followed by gravity filtration and dilution of collected acid with 34 mL H$_2$O (18 MQ). The collected effluent was analyzed using a Shimadzu 2010 GC equipped with three Restek columns (Rtx-1, RT-Msieve 5A, and RT-Q-Bond) and a thermal conductivity detector (TCD) as well as a flame ionization detector (FID). The carbon balance of each data point closes within 2%.

Equations

Propane conversion, $X$, is calculated as follows:

$$X = \sum \frac{F_{\text{carbon, prod}}}{F_{\text{C}_{3}\text{H}_{8}}},$$

where $F_{\text{carbon, prod}}$—flow of all carbon from products out of reactor (mol s$^{-1}$ g-cat$^{-1}$)

$F_{\text{C}_{3}\text{H}_{8}}$—flow of propane into the reactor (mol s$^{-1}$ g-cat$^{-1}$)

Product selectivity, $S$, is calculated as follows:

$$S = \frac{F_{\text{C}_{3}\text{H}_{8}, \text{out}}}{F_{\text{C}_{3}\text{H}_{8}, \text{in}}}$$

where $F_{\text{C}_{3}\text{H}_{8}, \text{out}}$—flow of carbon in product A out of reactor (mol s$^{-1}$ g-cat$^{-1}$)

$F_{\text{C}_{3}\text{H}_{8}, \text{in}}$—flow of all carbon from products out of reactor (mol s$^{-1}$ g-cat$^{-1}$)

Inverse weight-hour-space-velocity, WHSV$^{-1}$ (kg-cat s mol C$_3$H$_8$$^{-1}$), is calculated as follows:

$$\text{WHSV}^{-1} = \frac{M_{\text{cat}} \times (V/n)_{\text{STP}}}{F_{\text{C}_{3}\text{H}_{8}} \times N_{\text{C}_{3}\text{H}_{8}}},$$

where $M_{\text{cat}}$—mass of catalyst loaded in reactor (kg)

$(V/n)_{\text{STP}}$—24.5 (L/mol) at 298.15 K

(1 atm, R=8.206*10$^{-2}$ L atm K$^{-1}$ mol$^{-1}$)

$F_{\text{C}_{3}\text{H}_{8}}$—total flow of all inlet gasses (L s$^{-1}$)

$N_{\text{C}_{3}\text{H}_{8}}$—mol percent propane in gas feed (mol %)

Example 6: Nickel Boride as an Additional Active Catalysts for ODHP

In this example, we extend the ODHP catalyst assays disclosed in Example 4 to further include Ni-boride. As outlined in Example 4, various boron- or nitride-containing catalysts were screened for oxidative propane dehydroge-
nation (ODHP) activity, including B-nitride, Ti-nitride, Al-nitride, B-carbide, Ti-boride, and Nb-boride. In this example, we also demonstrate the catalytic activity of Ni-boride activity.

Operating conditions were as follows: \( P_{02} = 0.15 \) atm, \( P_{C3H8} = 0.3 \) atm, \( P_{N2} = 0.55 \) atm, T = 490°C. Due to differences in the reactivity between catalysts, total inlet flow rates between catalysts fluctuated between 40 and 140 mL min\(^{-1}\), in order to achieve ~5% propane conversion. About 200 mg of boron- or nitride-containing catalysts 600-710 \( \mu \)m in size were loaded in a 9 mm inner diameter quartz reactor. All carbon balances close to within ±5%.

All the tested boron- or nitride-containing catalysts, including Ni-boride, showed activity for ODHP. Furthermore, all the tested boron-containing catalysts, including Ni-boride, display high selectivity to propene, with the primary byproduct being ethylene.

Inlet flow rates of the \( C_3H_8/O_2/N_2 \) gas mixture past the screened boron-containing, nitride-containing and \( V/SiO_2 \) catalysts were varied to achieve a range of propane conversions. Operating conditions were as follows: \( P_{02} = 0.15 \) atm, \( P_{C3H8} = 0.3 \) atm, \( P_{N2} = 0.55 \) atm, T = 490°C. About 200 mg of boron- or nitride-containing catalysts 600-710 \( \mu \)m in size were loaded in a 9 mm inner diameter quartz reactor with total inlet flow rates of 40-140 mL min\(^{-1}\), equivalent to WHSV\(^{-1}\) of 100-300 kg-cat m\(^{-3}\). All carbon balances close to within ±5%.

As shown in FIG. 15, the boron-containing catalysts, including Ni-boride, maintained high propene selectivity even at high propane conversions. In sum, this example provides additional data supporting the Example 4 conclusion that a variety of boron- and nitride-containing catalysts can be used to catalyze the oxidative dehydrogenation of short chain alkanes to corresponding olefins.

Example 7: Selective Oxidative Dehydrogenation of n-Butane to 1-Butene and 2-Butene Using BNNTs

In this example, we demonstrate BNNT-catalyzed ODH using n-butane as the alkane reactant, resulting in a mixture of alkene products, 1-butene and 2-butene. The results demonstrate that the disclosed methods are not limited to ODH of propane (ODHP), but can instead be generalized to ODH of other alkanes to yield the corresponding alkenes.

In the ODH of n-butane, n-butane is dehydrogenated in the presence of oxygen to yield a mixture of 1-butene and 2-butene. Water is also produced. As noted previously, ODH produces undesirable byproducts, such as CO and CO\(_2\); thus, ODH catalysts demonstrate increased selectivity towards the desired alkene product (in this case, isobutene) are preferred.

Using the general methods outlined in the previous examples (see, e.g., Example 1 and Example 5), we assayed the ODH catalytic activity of both h-BN and BNNTs, along with \( V/SiO_2 \), a known isobutene ODH catalyst, using isobutane as the alkane reactant. Reaction conditions were: WHSV\(^{-1}\): 16-48 (kg-cats mol \( C_4H_{10} \)^{-1}) [\( V/SiO_2 \)]; 44-111 (kg-cats mol \( C_4H_{10} \)^{-1}) [h-BN]; 4-12 (kg-cats mol \( C_4H_{10} \)^{-1}) [BNNT]; T = 440°C, \( P_{02} = 0.1 \) atm, \( P_{C4H_{10}} = 0.1 \) atm (balance \( N_2 \)). The resulting ODH % conversion of isobutane and the product selectivities for each catalyst are shown in FIG. 18 (catalyst used on x-axis; isobutane conversion shown as black squares with values shown on the right side; selectivities shown as bars with values on the left side). As seen in FIG. 18, both BN materials (h-BN and BNNTs) show much higher selectivity to olefins than the traditional \( V/SiO_2 \) catalyst, which shows an undesirable high selectivity towards CO\(_2\) (~40%).

We plotted product selectivity as a function of isobutane conversion for the three ODH catalysts, and the results are shown in FIG. 19. Again, the results show that both h-BN and BNNT catalysts have higher selectivity for the favored olefin products (including, but not limited to, isobutene), and lower selectivity towards the undesired CO\(_2\) products than the conventional catalyst.

Example 8: Oxygen Functionalization of the BN Surface Increases Catalyst Activity

In this example, we demonstrate that the ODH-promoting activity of BN catalysts can be improved by bonding (i.e., functionalizing) oxygen to the BN surface. The BN surface can be functionalized with oxygen using one or more of a number of methods known in the art.

One such method is to contact the BN with nitric acid. We refluxed h-BN in concentrated HNO\(_3\) for 2 hours. The resulting oxidized BN material was recovered by vacuum filtration and dried in an oven overnight. We then investigated the catalytic activity of the resulting oxygen functionalized material using the oxidative dehydrogenation of propane (ODHP) reaction, as described generally in the previous examples (see, e.g., Example 5).

As seen in FIG. 20, the oxygen functionalized (HNO\(_3\)-treated) h-BN shows ~40% increase in the rate of propane consumption over an untreated h-BN material. XPS data confirms that the treated surface was in fact functionalized with oxygen. Specifically, the HNO\(_3\)-treated h-BN contains calcite, and NiMoO\(_3\). As seen in FIG. 17, BNNT shows comparable selectivity (see solid line) to the most selective previously reported n-butane catalysts.
3.83% (atom %) surface oxygen, while the untreated h-BN only contains 2.51% (atom %) surface oxygen.

In sum, this example demonstrates that the ODH catalytic activity of boron- and nitrile-containing catalyst can be further improved by bonding oxygen to (i.e., functionalizing with oxygen) the catalyst surface.

Example 10: BN Catalyzed Oxidative Dehydrogenation of Ethylbenzene

This example illustrates BN-catalyzed ODH using ethylbenzene as the alkyl group-containing reactant, resulting in styrene as the corresponding alkyl-group containing product. The results provide additional data demonstrating that the disclosed methods can be generalized to ODH of alkyl groups attached to an aromatic ring, to yield the corresponding alkyl group.

We were able to attain a saturated ethylbenzene feed into a quartz reactor by bubbling nitrogen through an ethylbenzene saturator kept heated at 50°C. The furnace of the quartz reactor tube could be varied to 250-500°C, while the surrounding atmosphere from the quartz reactor furnace was heated to 160°C. Stainless steel tubing from the liquid saturator to the reactor unit and the reactor unit to the gas chromatograph (GC) was kept heated at 220°C. Nitrogen flow through the saturator was kept constant at 50 mL min⁻¹, while O₂ flow was kept constant at 5 mL min⁻¹, to give overall feed concentrations as 9% O₂, 2.7% ethylbenzene (balance N₂).

The ethylbenzene conversion and product selectivity are displayed in Table 1, comparing the gas-phase reactions of a blank quartz reactor tube (only quartz wool) and a quartz tube containing h-BN. Even at 500°C, ethylbenzene conversion is marginal without h-BN present and increases to 27% conversion in the presence of h-BN, showing low selectivity to CO₂ and high selectivity to all other important products (mostly styrene, benzene, toluene).

TABLE 1

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Ethylbenzene Conversion [%]</th>
<th>Product Selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td></td>
<td>Styrene + Benzene + Toluene + Others</td>
</tr>
<tr>
<td>Blank</td>
<td>480</td>
<td>3.8</td>
</tr>
<tr>
<td>Tube</td>
<td>500</td>
<td>6.0</td>
</tr>
<tr>
<td>h-BN</td>
<td>500</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Example 11: Oxidative Coupling of Methane Using h-BN

This example illustrates the use of h-BN as catalyst for the oxidative coupling of methane (OCM) into ethane and ethylene products. The results show that the disclosed methods can be used for other types of oxidations beyond ODH.

In OCM, two methane molecules are coupled to form ethane and ethylene. During this process, water is also produced. The activation of methane requires significantly higher temperatures than ODH, typically above 700°C. These high temperatures lead to the over oxidation of reaction products into CO and CO₂. Thus, catalysts that can show activity (i.e. activating methane) while minimizing over oxidation products are desirable.

Using similar analytical methods as in the previous examples, we assayed the catalytic activity of h-BN and compared it with that of catalytically inert quartz chips. Any activity observed during the quartz chip experiment was deemed to originate from gas phase methane activation. To minimize gas phase reactions, quartz wool was used to fill the void space past the catalyst bed. The reaction conditions were: WHSV=1-9-14 (kg cat. mol CH₄⁻¹); T=750°C, 770°C; PO₂=0.20 atm, P_O₂^vent=0.4 atm (balance N₂).

The resulting OCM % conversion and selectivity towards coupling products (i.e. ethane and ethene) and COx products are shown in Table 2. At same flow rates and temperatures, the h-BN catalyst shows an increase in methane conversion of up to 55% when compared to the quartz chips. The h-BN catalyst's higher methane activation ability leads to a slightly lower C₂ selectivity due to the over oxidation of the ethane and ethylene products. Despite this loss of selectivity, the overall C₂ yields are higher than with the quartz chips.

TABLE 2

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Total Flow [mL/min]</th>
<th>OCM Conversion [%]</th>
<th>Product Selectivity [%]</th>
<th>C₂H₆/ C₂H₄ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz Chips</td>
<td>750</td>
<td>80</td>
<td>5.5</td>
<td>49.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.7</td>
<td>56.3</td>
<td>84.1</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>2.2</td>
<td>52.9</td>
<td>46.1</td>
</tr>
<tr>
<td></td>
<td>770</td>
<td>9.0</td>
<td>47.7</td>
<td>49.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.8</td>
<td>50.8</td>
<td>47.0</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>4.1</td>
<td>52.9</td>
<td>45.4</td>
</tr>
<tr>
<td>h-BN</td>
<td>750</td>
<td>80</td>
<td>13.2</td>
<td>46.1</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.2</td>
<td>44.5</td>
<td>53.4</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>4.8</td>
<td>44.9</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>770</td>
<td>80</td>
<td>20.1</td>
<td>37.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>12.6</td>
<td>43.3</td>
<td>54.2</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>8.5</td>
<td>46.6</td>
<td>51.4</td>
</tr>
</tbody>
</table>

Example 12: Selective Oxidative Dehydrogenation of Propane to Propene Using Elemental Boron Catalysts

In this example, we demonstrate that effective ODH catalysts can be made from different forms of elemental boron. Surprisingly, catalysts containing elemental boron exhibit substantially increased ODH productivity as compared to the h-BN and BNNT catalysts used in the previous examples, with a mixture of amorphous and crystalline boron (a/c-B) exhibiting the highest ODH productivity ever reported in the literature. Use of the a/c-B mixture resulted in a ~35-fold in the rate if propane consumption when compared to h-BN.

Materials for Examples 12-14

Compositions containing elemental boron were used as provided without further chemical or thermal treatment. Crystalline boron (c-B), supplied by Sigma Aldrich, was 99.7% pure, with a Brunauer-Emmett-Teller (BET) surface area of 1.0 m² g⁻¹. Amorphous boron (a-B), supplied by Strem Chemical, was 99% pure, with a BET surface area of 11.7 m² g⁻¹. The mixture of amorphous and crystalline boron (a/c-B), supplied by Alfa Aesar, was 98% pure, with...
a BET surface area of 11.2 m² g⁻¹. The impure amorphous boron containing 1% Mg and having oxygen as the major impurity (94% a-B, 1% Mg, O as major impurity), supplied by Alfa Aesar, had a BET surface area of 16.0 m² g⁻¹ and a 0.72 µm particle size (FN, from AA spectroscopy Certificate of Analysis). The impure amorphous boron containing 4% Mg (91% a-B, 4% Mg), supplied by Alfa Aesar, had a BET surface area of 11.9 m² g⁻¹ and a 0.73 µm particle size (FSSS) and a porosity of 0.82 (from AA spectroscopy Certificate of Analysis). The impure amorphous boron containing 4% Mg (91% a-B, 4% Mg), supplied by Alfa Aesar, had a BET surface area of 11.9 m² g⁻¹ and a 0.73 µm particle size (FSSS) and a porosity of 0.82 (from AA spectroscopy Certificate of Analysis). The h-BN and BNNTs used for comparison were sourced and treated as outlined in the previous examples.

Equations for Examples 12-14

Alkane conversion, X (%), is calculated as follows:

\[ X = \frac{\sum F_{\text{carbon prod}}}{F_{\text{alkane in}}} \times 100\% \]

where \( F_{\text{carbon prod}} \) = flow of all carbon products from reactor in mol s⁻¹ kgcat⁻¹

\( F_{\text{alkane in}} \) = flow of all alkane into the reactor in mol s⁻¹ kgcat⁻¹

Product selectivity, S (%), is calculated as follows:

\[ S = \frac{F_{\text{product out}}}{\sum F_{\text{carbon prod}}} \]

where \( F_{\text{product out}} \) = flow of product from reactor in mol s⁻¹ kgcat⁻¹

Carbon balance, defined as \( \sum F_{\text{carbon prod}} / F_{\text{alkane in}} \times 100\% \), where gas flow-rate.

Use of materials containing elemental boron results in a similar high selectivity to propane to that reported in the above examples using h-BN and BNNTs as catalysts, while also exhibiting substantially higher productivity. The high productivity and high melting point of elemental boron-containing catalysts may provide significant advantages over using the previously disclosed boron nitrides.

First, crystalline elemental boron (c-B) in three different quantities (42.0 mg c-B with QC, 77.5 mg c-B without QC, 300.0 mg c-B without QC) was used as a catalyst for ODHP. h-BN and BNNT catalysts were also used for comparison. The reaction parameters were T=490° C.; \( P_{C3H8}=0.30 \) atm; \( P_{O2}=0.15 \) atm; \( P_{N2}=0.55 \) atm; and flow (F)=40-170 mL min⁻¹. As seen in FIG. 21, the results illustrate that crystalline elemental boron catalyzes ODHP with a selectivity that is comparable to h-BN and BNNTs. As shown in FIG. 22, the major side product of c-B catalyzed ODHP is ethylene. As seen in FIG. 23, the product distribution for c-B catalyzed ODHP is comparable to the distribution obtained using h-BN and BNNT catalysts.

Similar experiments were performed with the same reaction parameters using a mixture of both crystalline and non-crystalline (amorphous) boron (a/c-B) as the ODHP catalyst. As seen in FIG. 24, the amorphous/crystalline boron mixture produces a conversion (X) vs. selectivity (S) line that is almost identical to that of the crystalline boron catalyst.

Next, rate comparison and productivity calculations were performed using the data obtained using the a/c-B, c-B, h-BN and BNNT catalysts. Use of the a/c-B catalyst resulted in a consumption rate of 11.8x10⁻² molc₃H₈ kgcat⁻¹ s⁻¹. Use of the c-B catalyst resulted in a consumption rate of 3.5x10⁻² molc₃H₈ kgcat⁻¹ s⁻¹. Use of the BNNT catalyst resulted in a consumption rate of 3.5x10⁻² molc₃H₈ kgcat⁻¹ s⁻¹. As further shown in FIG. 25, both forms of elemental boron exhibited a substantially increased rate of propane consumption, as compared to the two boron nitride catalysts, with the a/c-B demonstrating a ~35-fold increase in the rate of propane consumption, as compared to h-BN.

As seen in FIG. 26, both a/c-B and c-B exhibited substantially higher productivity than either of the boron nitride catalysts. Notably, a/c-B is twice as productive as c-B, and substantially more productive than any previously reported ODHP catalyst. Higher productivity can facilitate a reduction in reactor diameters, thus reducing capital costs in scaling this technology. Furthermore, the high melting point of elemental boron offers long-term stability of such catalysts.

Further experiments were performed under the same reaction parameters (T=490° C.; \( P_{C3H8}=0.30 \) atm; \( P_{O2}=0.15 \) atm; \( P_{N2}=0.55 \) atm; flow (F)=40-170 mL min⁻¹; WHSV⁻¹=0.6-6.6 kgc₃H₈ mol⁻¹ s⁻¹; carbon balance +/-3%) using three different compositions containing elemental boron (99% amorphous boron, a-B; 94-96% amorphous boron with 1% Mg and O as the major impurity; and 91% amorphous boron with Mg as the major impurity) in addition to the c-B and the a/c-B used previously. 20 mg of the catalysts having an amorphous component were loaded in 380 mg quartz chips, and 40 mg of the crystalline boron catalysts were loaded in 360 mg quartz chips. As seen in FIG. 27, selectivity to propylene and all olefins was similar for all of the elemental boron-containing catalysts.
Comparison of propane ODH productivity using the five elemental boron-containing catalysts ODH1, catalyst and the two boron nitride-containing catalysts again confirms that the elemental boron-containing catalysts exhibit substantially increased productivity as compared to the two boron nitride-containing catalysts (FIG. 28). Notably, the substantially pure boron compositions (e-B, a-B and a/c-B, 98+% pure) exhibited higher productivity than the two impure boron compositions.

In summary, example 1 identifies compositions containing elemental boron as a hitherto unexplored oxidation catalyst. High selectivity towards propane with substantially improved productivity were exhibited when such compositions were used to catalyze the oxidative dehydrogenation of propane.

Example 13: Selective Oxidative Dehydrogenation of Ethane, Isobutane, and n-Butane Using Elemental Boron

This example illustrates elemental boron-catalyzed ODH using ethane, isobutane and n-butane as the alkane reactants, resulting in ethylene, isobutene, and various n-butenes, respectively, as the alkene products. The results provide additional data demonstrating that the disclosed methods using elemental boron catalysts can be generalized to ODH of a variety of alkanes to yield the corresponding alkenes.

Using the general methods outlined in the previous examples (see, e.g., Example 1, Example 5 and Example 6), we assayed the ODH catalytic activity of amorphous elemental boron (a-B, Strem) using ethane, isobutane, and n-butane as the alkane reactants. 40 mg a-B was loaded in 360 mg quartz chips with a flow stream of gases (PC2H6=0.10 atm; PN2=0.80 atm; P02=0.15 atm; P02=0.20 atm; P02=0.40 atm) at two different temperatures (T=750° C. and 770° C.) and six different flow rates (60, 80, 100, 120, and 140 mL/min). Carbon balance was +/-2%. The results are shown in Table 3 below.

TABLE 2

<table>
<thead>
<tr>
<th>Flow (mL/min)</th>
<th>WHSV−1 (kgca<em>s−1</em>mol−1)</th>
<th>CH4 conversion (%)</th>
<th>C2H6 selectivity (%)</th>
<th>C2H4 selectivity (%)</th>
<th>C2 selectivity (%)</th>
<th>yield (%)</th>
<th>CO selectivity (%)</th>
<th>CO2 conversion ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 750° C.</td>
<td>60 2.6 32.9 5.1 16.1 21.2 6.9 6.2 82.0</td>
<td>80 1.9 27.5 7.1 18.4 25.5 7.0 7.9 65.9</td>
<td>100 1.6 21.9 9.7 19.9 29.6 6.5 10.0 50.2</td>
<td>120 1.3 17.5 12.5 20.4 32.8 5.7 12.1 38.7</td>
<td>140 1.1 14.2 15.0 20.3 35.2 5.0 13.6 31.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T = 770° C.</td>
<td>60 2.6 36.4 4.0 15.6 19.7 7.2 5.9 90.4</td>
<td>80 1.9 33.2 5.1 17.1 22.2 7.4 6.8 81.2</td>
<td>100 1.6 29.2 6.7 18.8 25.4 7.4 8.2 68.9</td>
<td>120 1.3 25.2 8.5 20.2 28.6 7.2 9.9 57.2</td>
<td>140 1.1 19.4 11.3 21.7 33.0 6.4 12.5 46.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These results demonstrate that elemental boron is an effective catalyst for the oxidative dehydrogenation of methane. The invention is not limited to the embodiments set forth in this disclosure for illustration, but includes everything that is within the scope of the claims. Furthermore, all documents cited in this disclosure are hereby incorporated by reference in their entirety and for all purposes as if fully set forth in this disclosure.

We claim:

1. A method of making one or more desired chemical products, comprising contacting a heterogeneous catalyst consisting essentially of elemental boron with oxygen and one or more liquid or gaseous reactants, whereby the heterogeneous catalyst catalyzes the oxidative dehydrogenation (ODH) of the one or more liquid or gaseous reactants or oxidative coupling of methane (OCM) to form the one or more desired chemical products.

2. The method of claim 1, wherein:
   (a) the heterogeneous catalyst catalyzes the oxidative dehydrogenation (ODH) of the one or more liquid or gaseous reactants;
   (b) the one or more liquid or gaseous reactants include an alkane or a hydrocarbon comprising an alkyl group; and
(c) the one or more desired chemical products include one or more olefins or one or more hydrocarbons comprising an alkenyl group.

3. The method of claim 2, wherein the one or more liquid or gaseous reactants include an alkane.

4. The method of claim 3, wherein the alkane is a \( \text{C}_2-\text{C}_5 \) n-alkane or \( \text{C}_3-\text{C}_4 \) iso-alkane.

5. The method of claim 4, wherein the alkane is a \( \text{C}_2-\text{C}_4 \) n-alkane or \( \text{C}_3-\text{C}_4 \) iso-alkane.

6. The method of claim 5, wherein the \( \text{C}_2-\text{C}_4 \) n-alkane or \( \text{C}_3-\text{C}_4 \) iso-alkane is selected from the group consisting of ethane, propane, n-butane, and isobutane, and wherein the one or more desired chemical products are selected from the group consisting of ethene, propene, isobutene, n-butene, and butadiene.

7. The method of claim 6, wherein the \( \text{C}_2-\text{C}_4 \) n-alkane is propane and the desired chemical product is propene.

8. The method of claim 7, wherein the one or more liquid or gaseous reactants include methane, the heterogeneous catalyst catalyzes the oxidative coupling of methane, and the one or more desired chemical products include ethane and/or ethylene.

9. The method of claim 8, wherein the heterogeneous catalyst is contacted with natural gas.

10. The method of claim 1, wherein the elemental boron is in the form of crystalline boron (c-B), amorphous boron (a-B), or a mixture of amorphous and crystalline boron.

11. The method of claim 1, wherein the heterogeneous catalyst is made up of (a) at least 90% elemental boron by weight, or (b) at least 98% elemental boron by weight.

12. The method of claim 1, wherein the Brunauer-Emmett-Teller (BET) surface area of the heterogeneous catalyst is from 0.50 to 550 m² g⁻¹.

13. The method of claim 12, wherein the heterogeneous catalyst has a surface area range of 0.70 m² g⁻¹ to 500 m² g⁻¹, 0.80 m² g⁻¹ to 200 m² g⁻¹, 0.90 m² g⁻¹ to 100 m² g⁻¹, or 1.0 m² g⁻¹ to 20 m² g⁻¹.

14. The method of claim 1, wherein the average particle size of the heterogeneous catalyst is from 0.20 to 1.5 µm.

15. The method of claim 1, wherein the contacting step occurs at a temperature of from 400° C. to 800° C.

16. The method of claim 1, wherein the oxygen and one or more liquid or gaseous reactants are in a reactant stream that is contacted with the heterogeneous catalyst.

17. The method of claim 16, wherein the reactant stream includes from 0% to 70% nitrogen by volume.

* * * * *