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(19) **United States**(12) **Patent Application Publication**
Schreier et al.(10) **Pub. No.: US 2026/0139389 A1**(43) **Pub. Date: May 21, 2026**(54) **ELECTROCHEMICAL DEHYDROGENATION****Publication Classification**(71) Applicant: **Wisconsin Alumni Research Foundation**, Madison, WI (US)(72) Inventors: **Marcel Schreier**, Madison, WI (US); **Gong Zhang**, Madison, WI (US); **Lee Fuller**, DeForest, WI (US)(73) Assignee: **Wisconsin Alumni Research Foundation**, Madison, WI (US)(21) Appl. No.: **19/396,967**(22) Filed: **Nov. 21, 2025****Related U.S. Application Data**

(60) Provisional application No. 63/723,194, filed on Nov. 21, 2024.

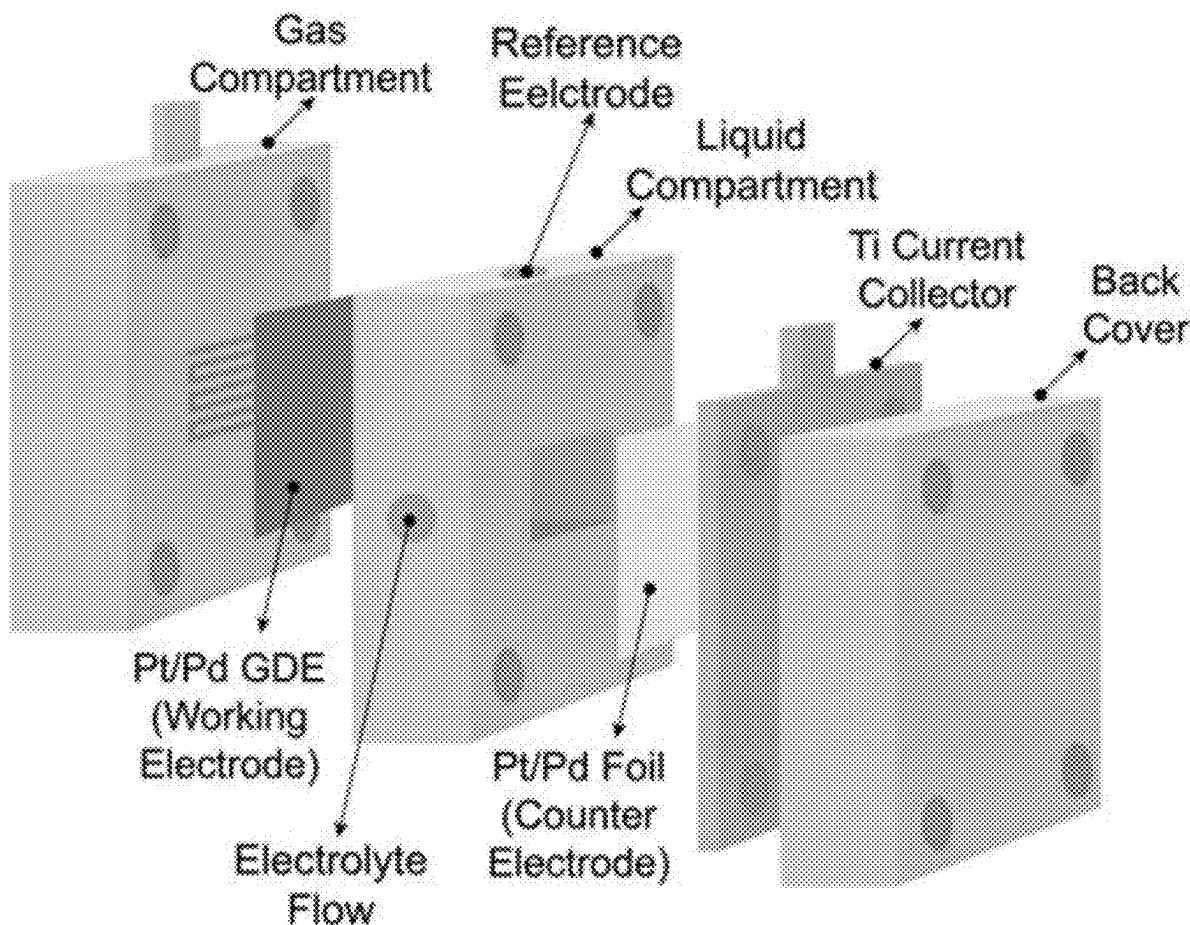
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(2021.01)

(57)

ABSTRACT

Methods of electrochemically dehydrogenating chemical reactants to generate dehydrogenated products, such as olefins. The methods can include adsorbing a chemical reactant to an electrode, dehydrogenating the adsorbed chemical reactant to yield an adsorbed dehydrogenated product, and desorbing the adsorbed dehydrogenated product to yield a dehydrogenated product by applying various electrical potentials to the electrode without the need to employ extreme temperatures and pressures.



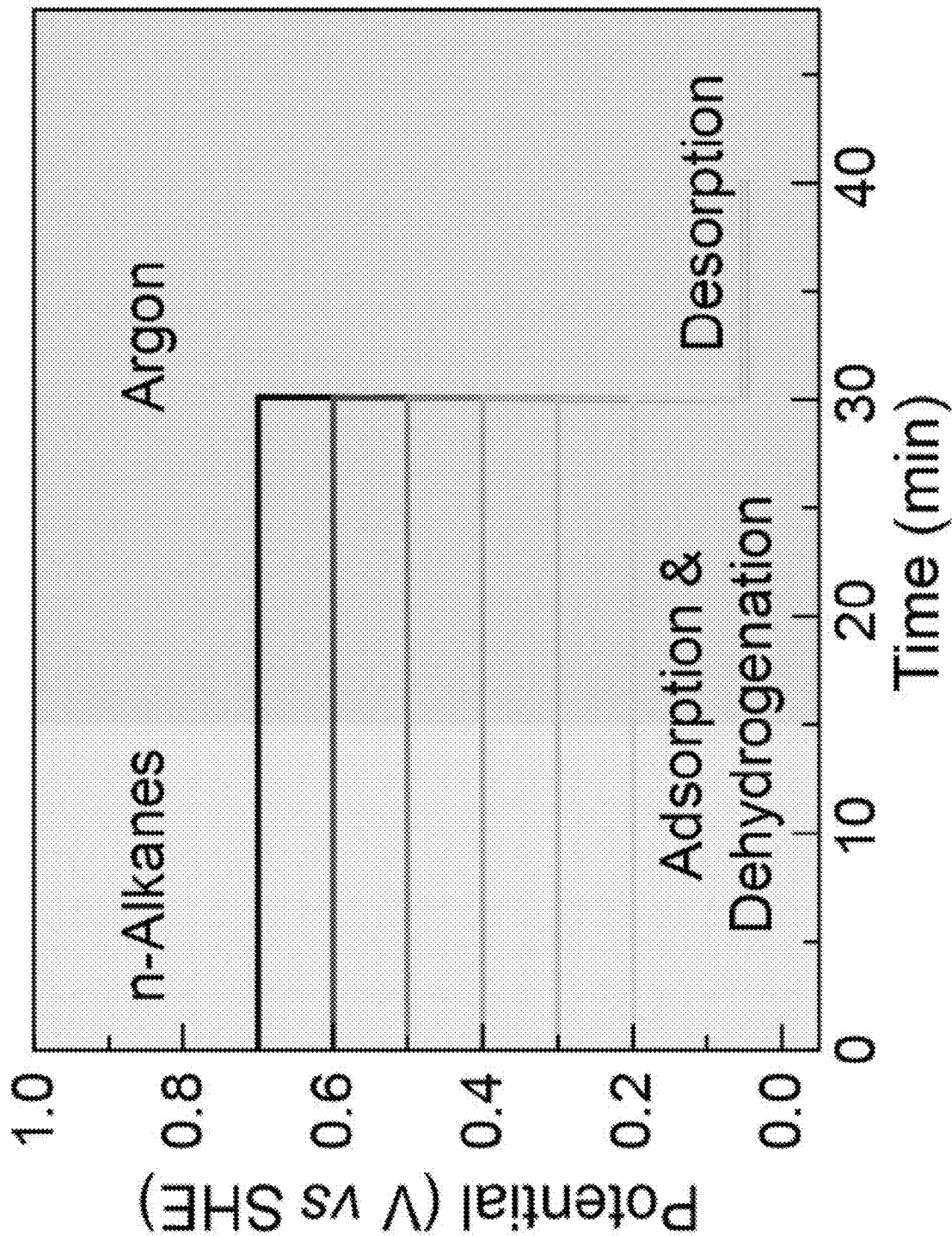


Fig. 1

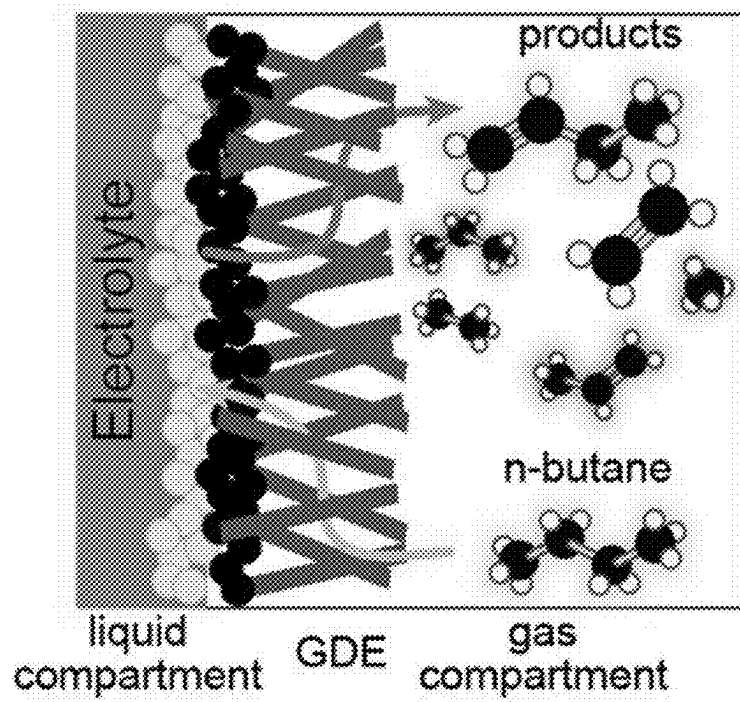


Fig. 2A

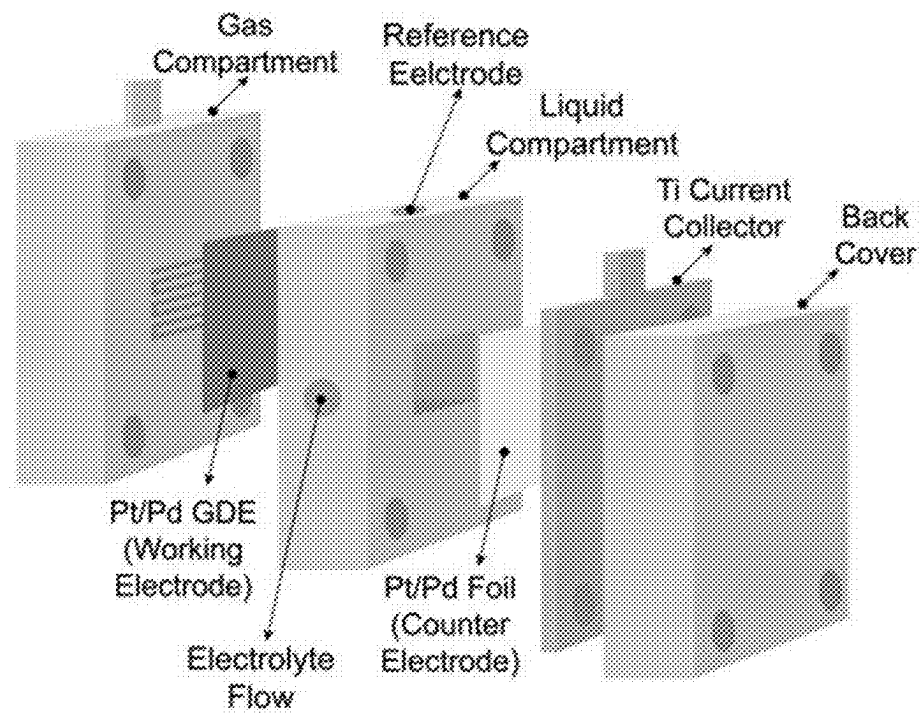


Fig. 2B

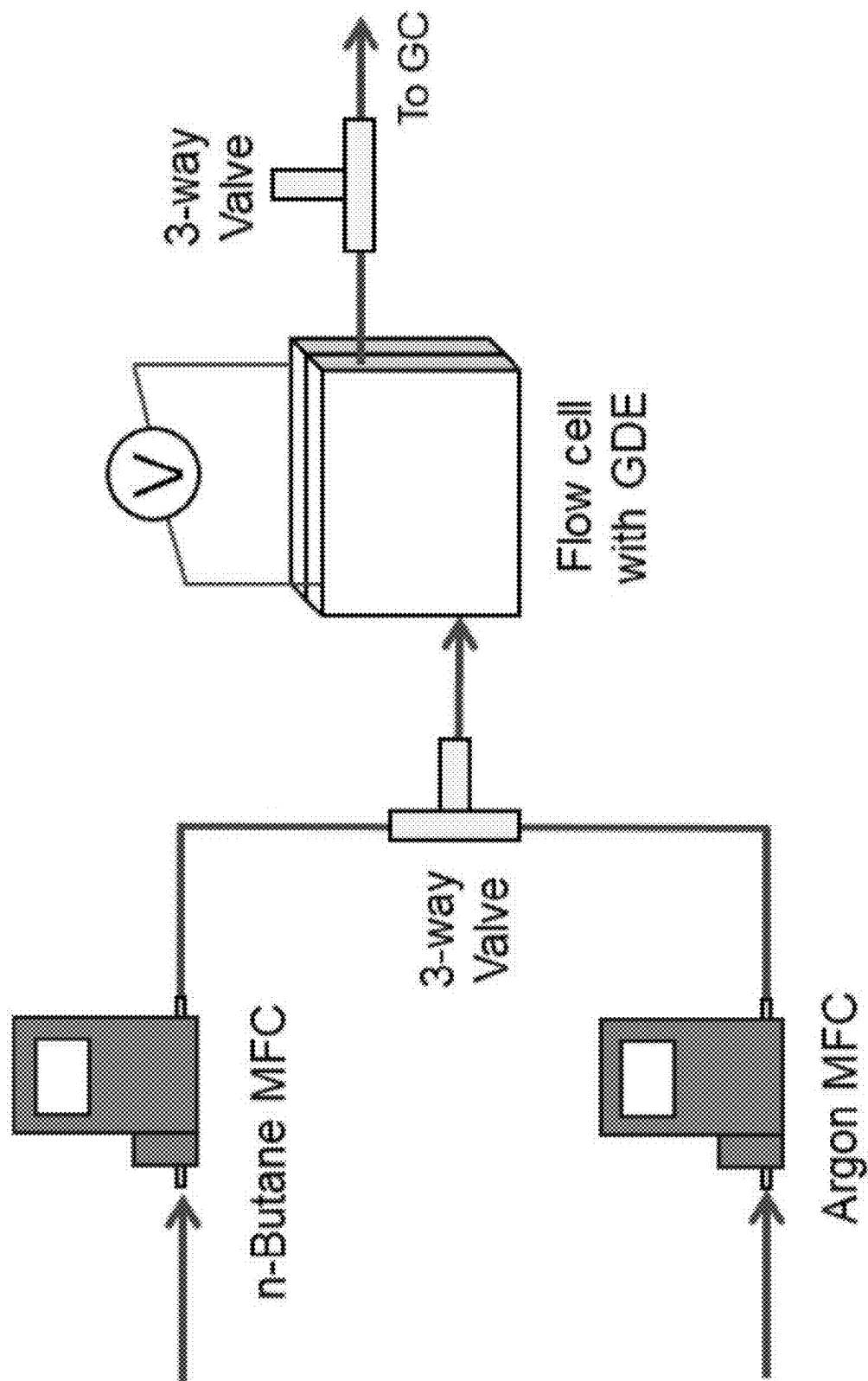


Fig. 3

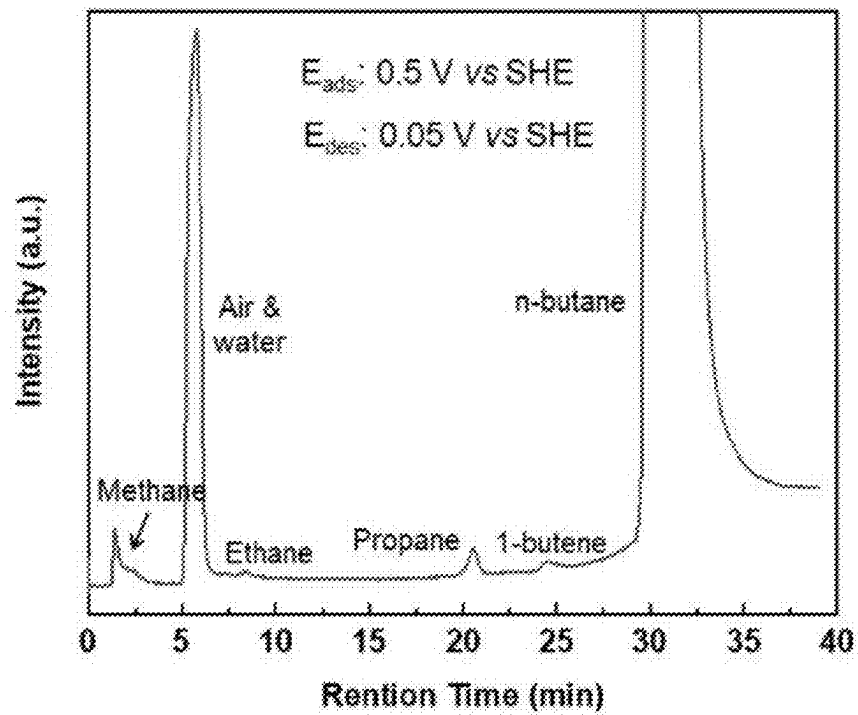
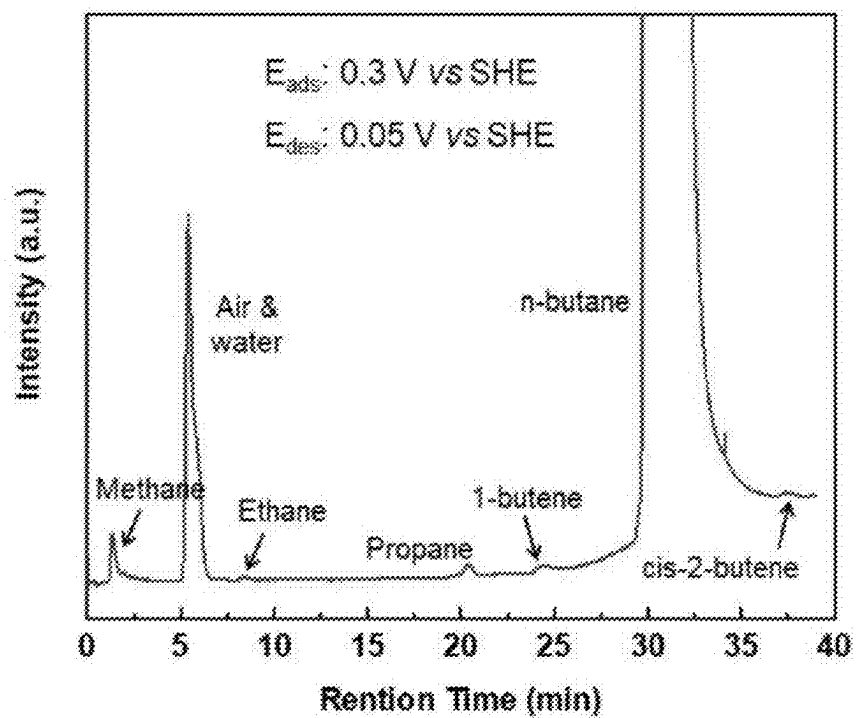


Fig. 4

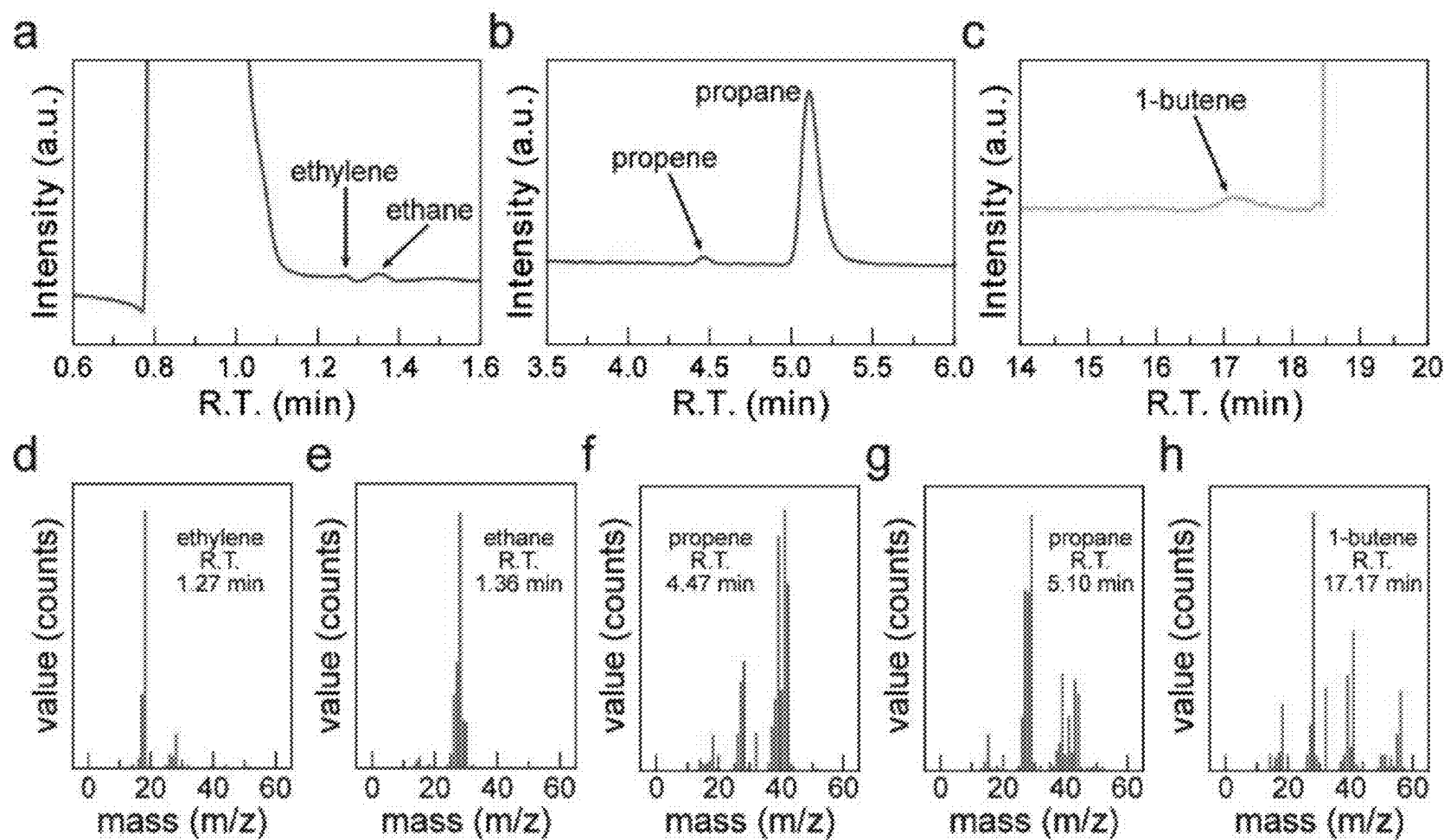


Fig. 5

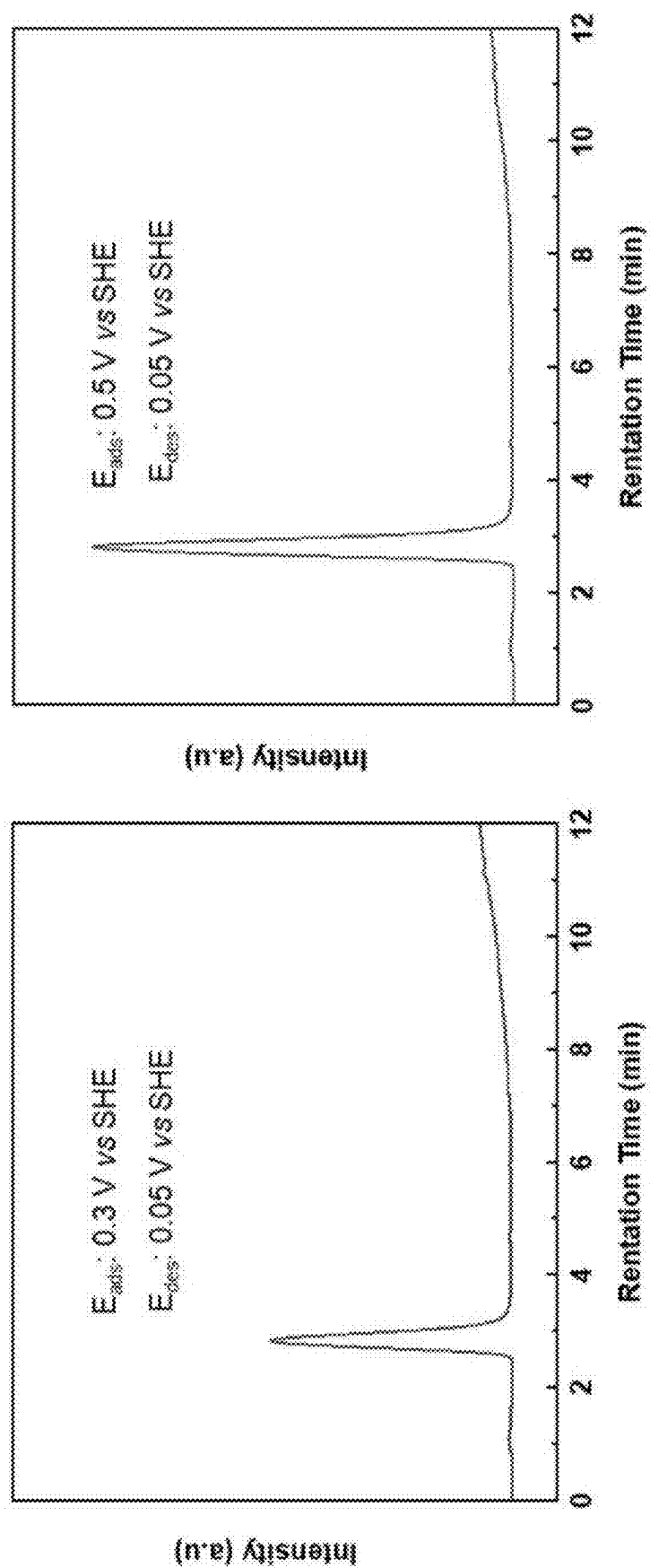


Fig. 6

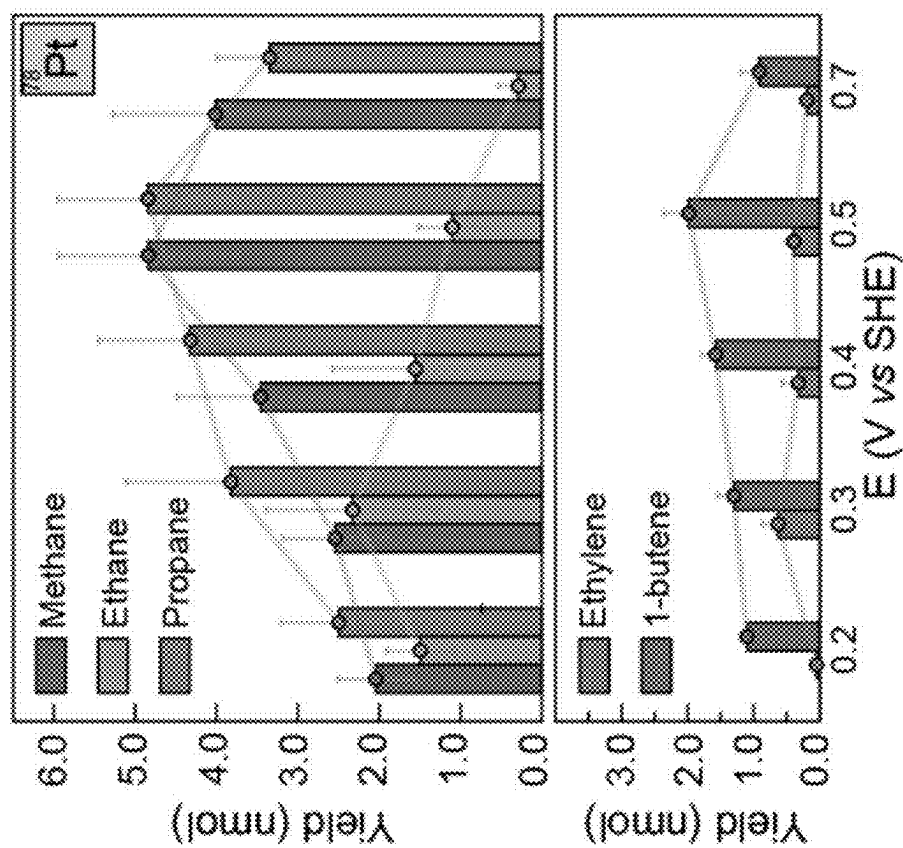


Fig. 7B

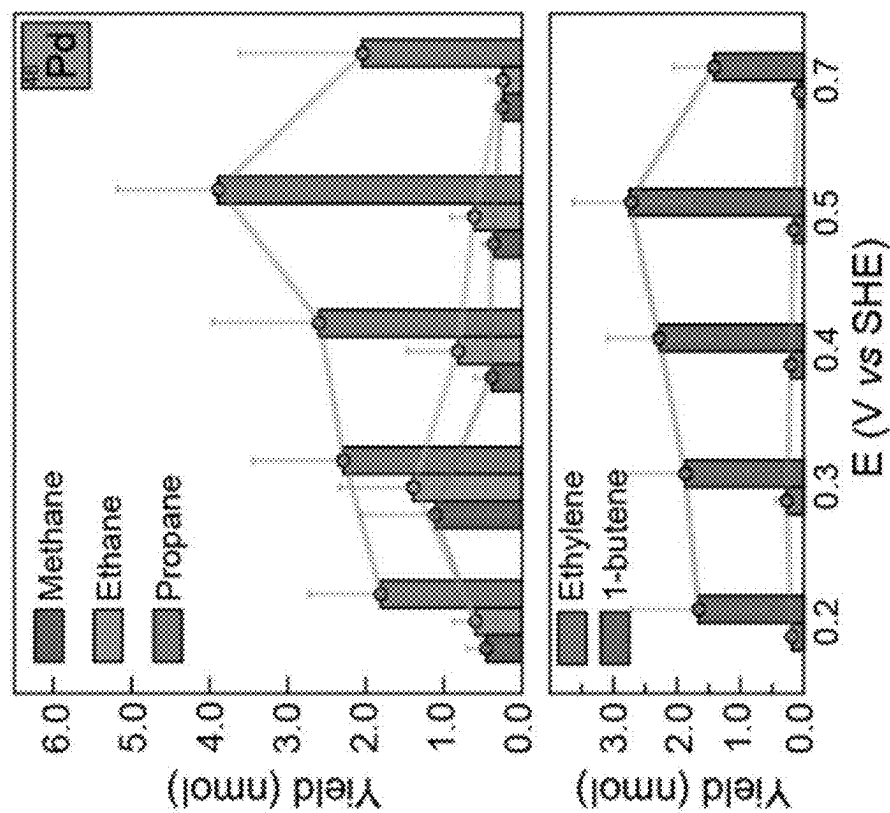


Fig. 7A

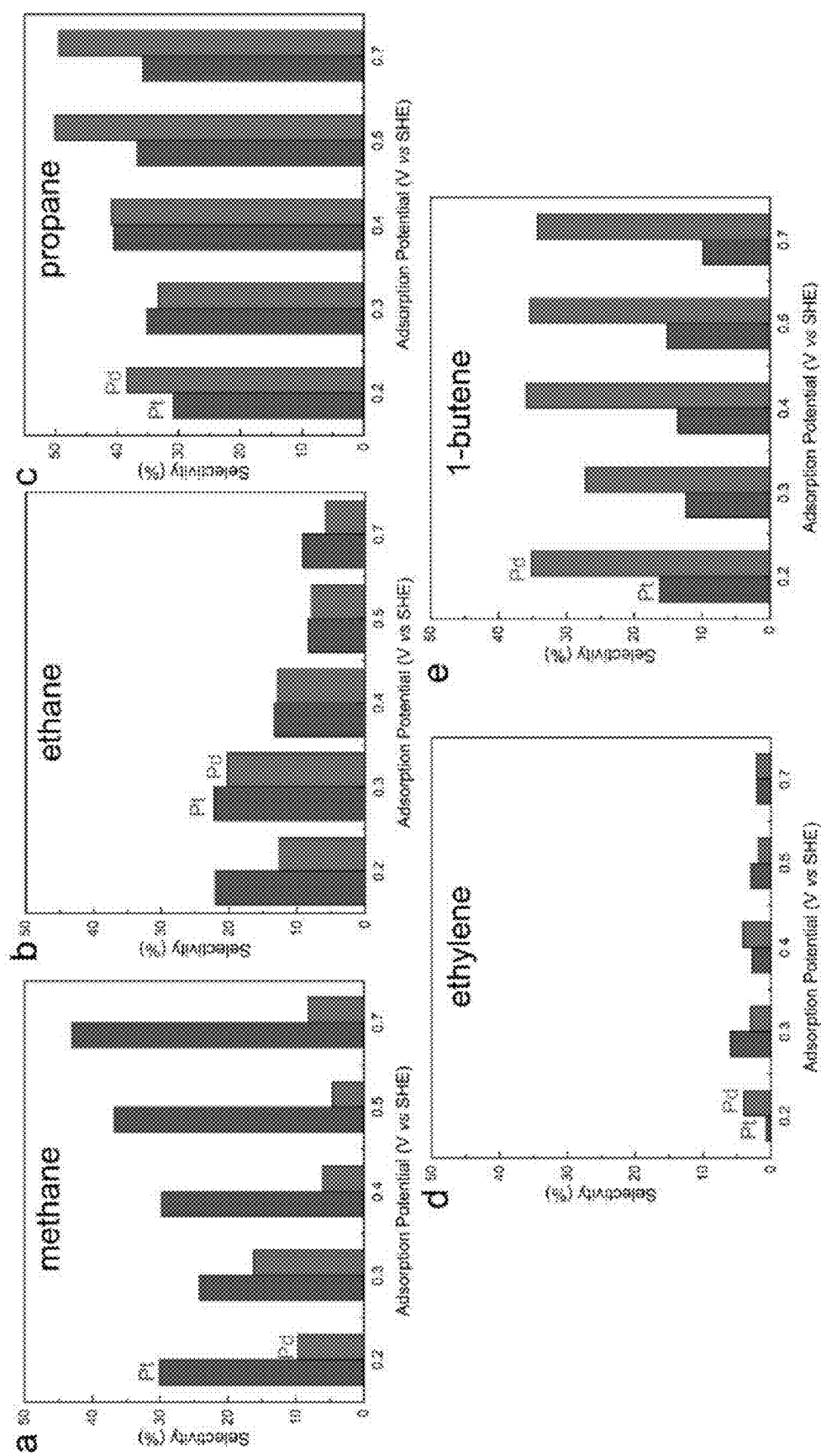


Fig. 8

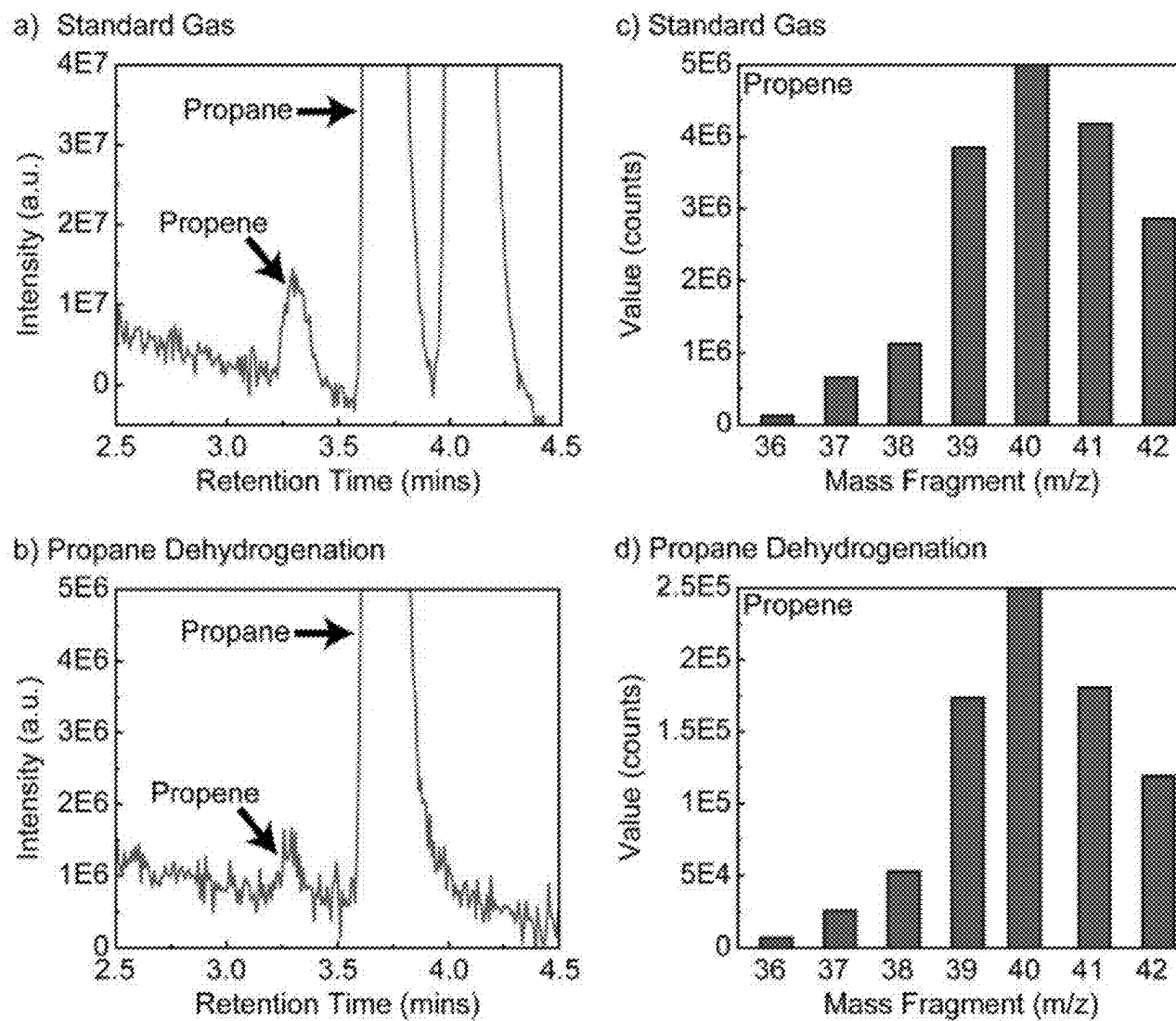


Fig. 9

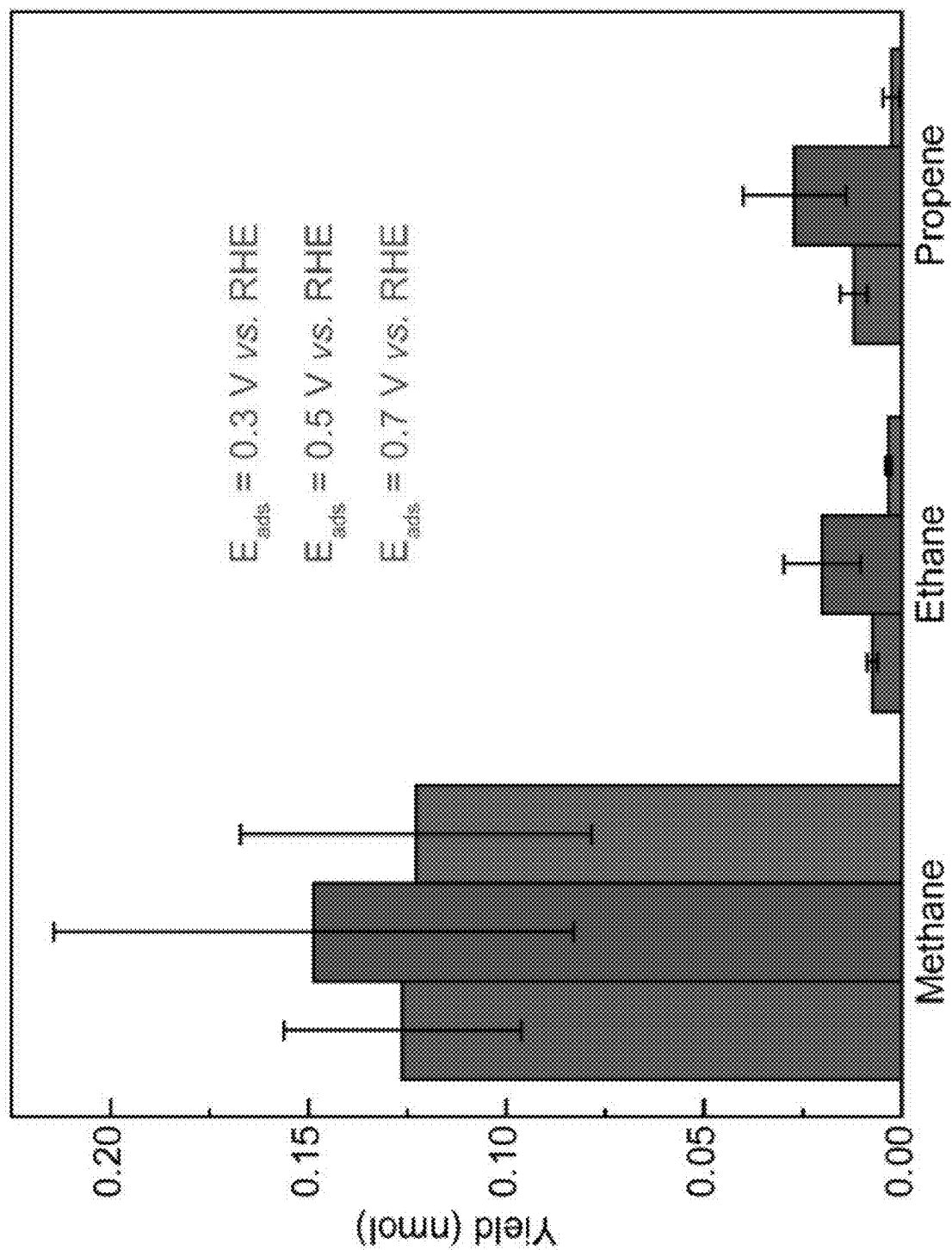


Fig. 10

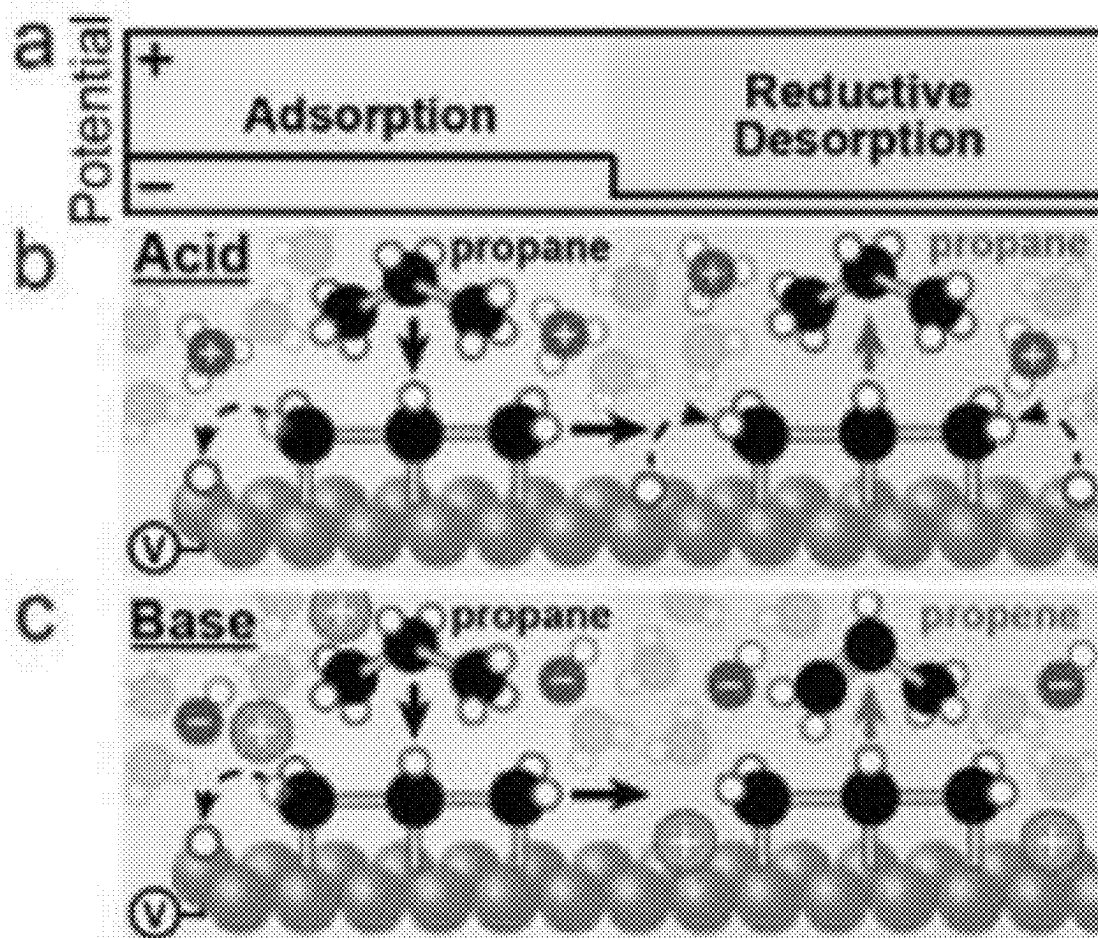


Fig. 11

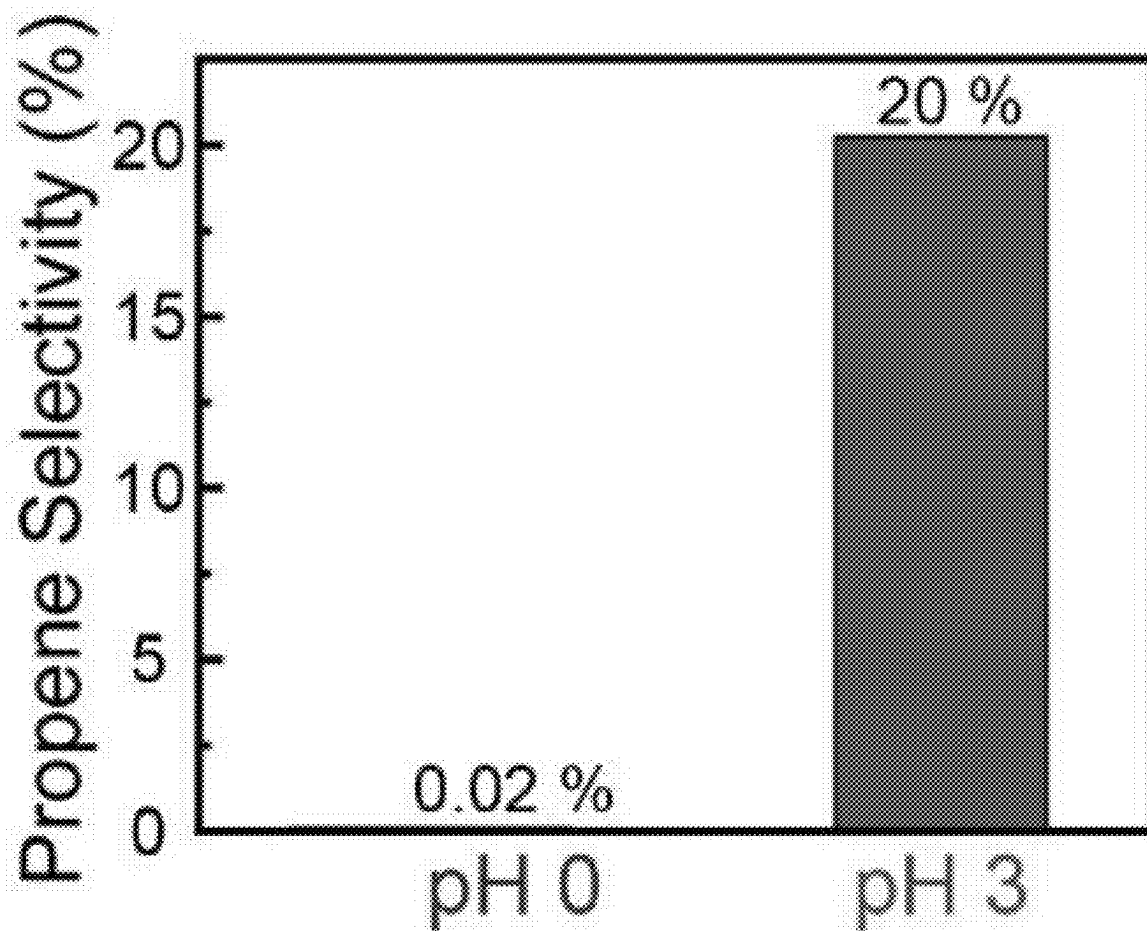


Fig. 12

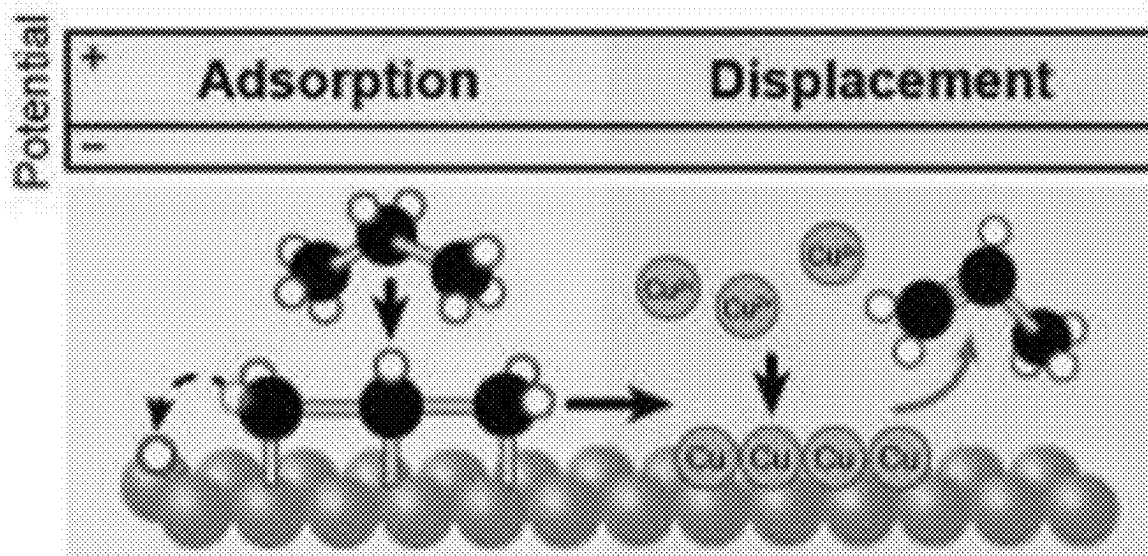


Fig. 13

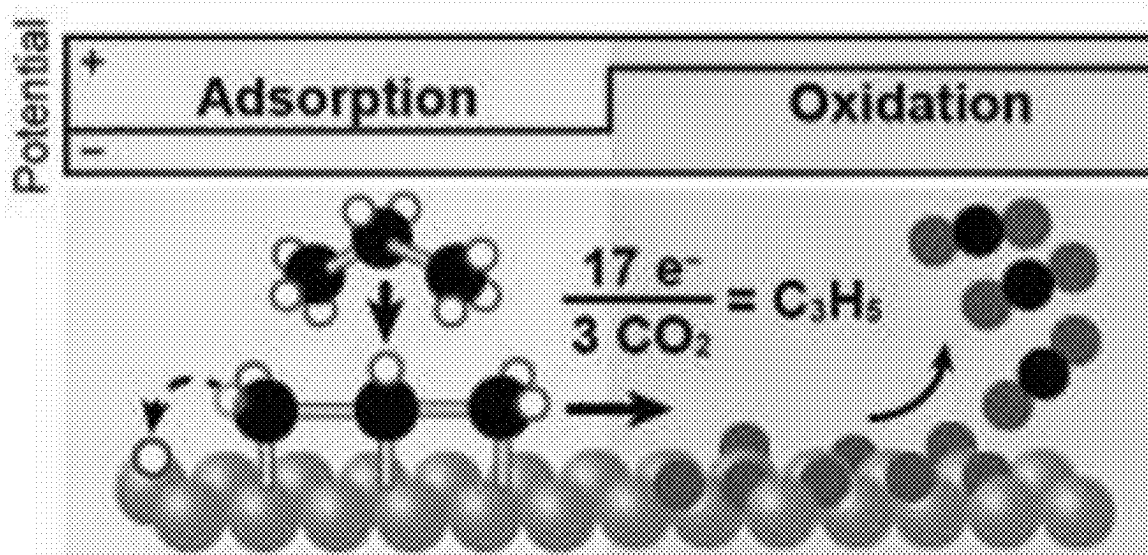


Fig. 14

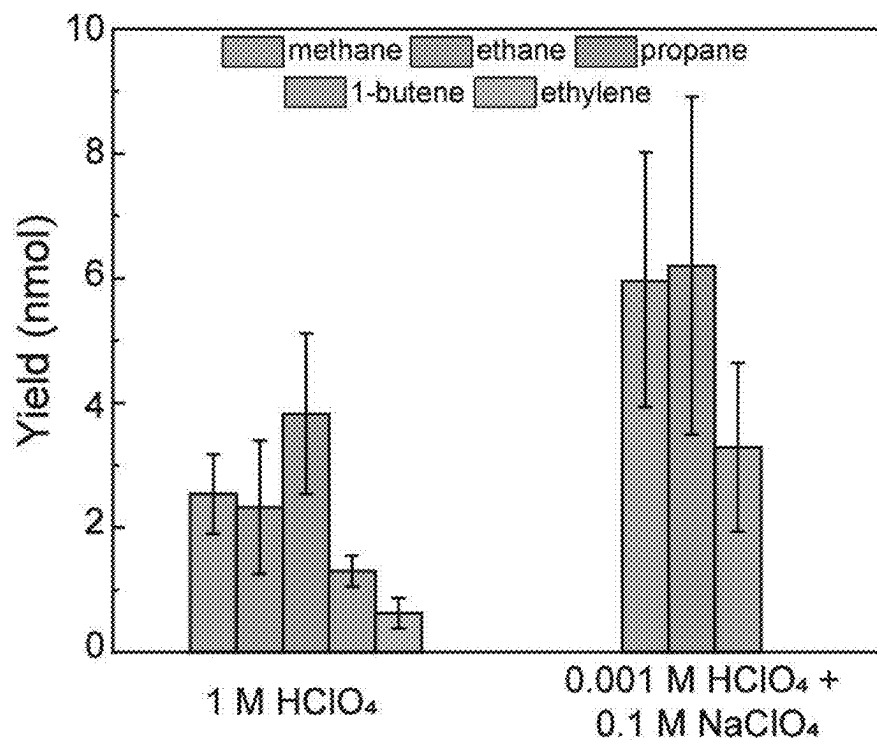


Fig. 15

ELECTROCHEMICAL DEHYDROGENATION**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] Priority is hereby claimed to co-pending provisional application Ser. No. 63/723,194, filed Nov. 21, 2024, which is incorporated herein by reference.

FEDERAL FUNDING STATEMENT

[0002] This invention was made with government support under 2338627 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

[0003] Short-chain alkenes (≤ 6 carbon atoms) such as ethylene, propene, butene, and butadiene are essential raw materials for producing synthetic fibers, rubbers, plastics, and various other products. Traditionally, most global multi-carbon olefin production has relied on cryogenic extractive distillation from naphtha steam cracking. However, with the increasing availability of inexpensive shale gas, there is growing interest in the direct dehydrogenation of alkanes from shale gas liquid fractions.

[0004] The most established industrial technology for n-alkane dehydrogenation is the CATADIENE® process (Lummus Technology, Houston, TX), which uses chromium oxide-based catalysts and operates at temperatures between 600 and 680° C. under sub-atmospheric pressure. This method requires continuous catalyst regeneration to burn off coke deposits. However, chromium oxide catalysts present environmental and health risks due to their toxicity. Others have developed a modified version of the Phillips Triolefin Process employing a platinum catalyst. However, its widespread adoption has been limited by high costs and process complexity. Similarly, others have proposed a process that introduces halogens as hydrogen acceptors to remove hydrogen from the product and shift the reaction equilibrium favorably. This method, however, is not yet commercially available and poses equipment corrosion issues. In conclusion, the current one-step direct n-alkane dehydrogenation processes are hindered by high energy consumption, unsustainability, and increased carbon emissions.

[0005] New methods for producing olefins, such as dehydrogenation at ambient temperature and pressure, are needed.

SUMMARY

[0006] Disclosed herein are methods of electrochemically dehydrogenating chemical reactants to generate dehydrogenated products. The methods can be performed at ambient temperature and atmospheric pressure.

[0007] Specifically, disclosed and claimed herein is a method of dehydrogenating chemical reactant comprising one or more C—H bonds to yield dehydrogenated product, the method comprising:

[0008] (a) introducing the chemical reactant to an electrode of an electrochemical cell;

[0009] (b) adsorbing at least a portion of the chemical reactant to the electrode by applying an adsorption potential to the electrode to thereby yield adsorbed chemical reactant comprising one or more C—H bonds;

[0010] (c) dehydrogenating at least a portion of the adsorbed chemical reactant by applying a dehydrogenation potential (which is the same as or different from the adsorption potential) to the electrode for a time effective to break at least one of the C—H bonds in at least a portion of the adsorbed chemical reactant to thereby yield adsorbed dehydrogenated product; and

[0011] (d) desorbing at least a portion of the adsorbed dehydrogenated product from the electrode by applying a desorption potential to the electrode to thereby yield the dehydrogenated product.

[0012] In some embodiments, at least one species of the adsorbed chemical reactant comprises one or more C—C bonds. The at least one species may comprise a C₃ or C₄ hydrocarbon species. In some such embodiments, the dehydrogenating breaks at least one of the C—H bonds without breaking any of the C—C bonds in at least 0.01% by number of the at least one species of the adsorbed chemical reactant. In some such embodiments, the dehydrogenation potential is other than a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in the at least one species. In some such embodiments, the dehydrogenation potential is not within ± 0.05 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in the at least one species. In some such embodiments, the dehydrogenation potential is a potential within ± 0.05 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species. In some such embodiments, the dehydrogenation potential is a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species.

[0013] In some embodiments, the adsorption potential and the dehydrogenation potential are greater than a potential of zero charge of the electrode. In some embodiments, the adsorption potential and the dehydrogenation potential are from about 0.1 V to about 1 V relative to a standard hydrogen electrode.

[0014] In some embodiments, the desorption potential is less than the adsorption potential and the dehydrogenation potential. In some embodiments, the desorption potential is less than a potential of zero charge of the electrode. In some embodiments, the desorption potential is within an under-potential deposition range for hydrogen (H_{UPD}) on the electrode. In some embodiments, the desorption potential is less than 0.09 V relative to a standard hydrogen electrode (SHE).

[0015] In some embodiments, the chemical reactant comprises a saturated hydrocarbon, an unsaturated hydrocarbon, or a polymer whose backbone comprises carbon atoms. In some embodiments, the chemical reactant comprises a C₂-C₁₂ linear, branched, or cyclic alkane, an addition polymer, a condensation polymer, or any combination thereof. In some embodiments, the chemical reactant is selected from the group consisting of ethane, and linear, branched, or cyclic propane, butane, pentane, octane, and any combination thereof.

[0016] In some embodiments, the dehydrogenated product comprises a C₂-C₁₂ alkene. In some embodiments, the dehydrogenated product comprises propene and/or butene.

[0017] In some embodiments, the adsorbing, the dehydrogenating, and the desorbing are conducted within a flow cell.

[0018] In some embodiments, the electrode is a gas diffusion electrode.

[0019] In some embodiments, the introducing the chemical reactant(s) comprises introducing the chemical reactant (s) in a gas phase feedstock. In still other versions of the method, the chemical reactant(s) can be introduced as a dissolved specie(s) in a solution.

[0020] In some embodiments, the electrode comprises one or more metals. In some such embodiments, the electrode comprises one or more metals selected from the group consisting of Pt, Au, Ag, Cu, Fe, Rh, Ni, Pd, Ir, Co, V, Cr, Sn, Ti, W, and alloys, sulfides, nitrides, oxides, and carbides thereof.

[0021] In some embodiments, the adsorbing, the dehydrogenating, and the desorbing are conducted at a temperature of from about 15° C. to about 30° C. In some embodiments, the adsorbing, the dehydrogenating, and the desorbing are conducted at a temperature of from about 15° C. to about 30° C., and without an externally applied source of heat other than the applied electrical potentials.

[0022] In some embodiments, the adsorbing, the dehydrogenating, and the desorbing are conducted at a pressure of from about 0.8 to about 1.2 atm.

[0023] In some embodiments, the electrode of the electrochemical cell is in contact with an electrolyte formulation and the electrolyte formulation comprises an ion selected from the group consisting of I^- , Cl^- , Cu^{2+} , Ce^{2+} , and CN^- .

[0024] In some embodiments, the electrode of the electrochemical cell is in contact with an electrolyte formulation and the electrolyte formulation comprises a reduced proton concentration relative to an acidic electrolyte. In some such embodiments, at least a portion of the protons in the electrolyte formulation is replaced with one or more cations selected from the group consisting of alkali metal cations and multivalent cations.

[0025] The objects and advantages of the disclosure will appear more fully from the following detailed description of the preferred embodiment of the disclosure made in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1. A schematic diagram illustrating exemplary potential switching employed in the present method.

[0027] FIGS. 2A-2B. Schematic diagrams of an exemplary reaction apparatus employed in the present method: (FIG. 2A) Schematic of the gas diffusion electrode structure; (FIG. 2B) Schematic of the flow cell. Not drawn to scale.

[0028] FIG. 3. Schematic diagram of exemplary gas line connections and devices used in the present method. A three-way valve ensures that only one gas flows through at a time. Not drawn to scale. MFC: mass flow controller. GDE: gas diffusion electrode.

[0029] FIG. 4. Exemplary chromatograms of desorption products corresponding to different adsorption potentials. a.u. arbitrary unit.

[0030] FIG. 5. Results of GC-MS experiments of n-butane dehydrogenation on a platinum GDE: (a) Total ion chromatography (TIC) of ethylene and ethane peaks; (b) TIC plot of propene and propane peaks; (c) TIC plot of the 1-butene peak; MS signals of (d) ethylene; (e) ethane; (f) propene; (g) propane and (h) 1-butene corresponding to different retention times. GDE: gas diffusion electrode. a.u. arbitrary unit. R.T., retention time.

[0031] FIG. 6. Exemplary chromatograms of oxidation products obtained during post-desorption cleaning. a.u. arbitrary unit.

[0032] FIGS. 7A-7B. Influence of adsorption potentials on n-butane adsorption and conversion: (FIG. 7A) Trends in n-butane conversion products as a function of adsorption potentials using platinum GDEs; (FIG. 7B) Trends in n-butane conversion products as a function of adsorption potentials using palladium GDEs.

[0033] FIG. 8. Comparison of the selectivity of n-butane conversion products between platinum and palladium electrodes at different adsorption potentials.

[0034] FIG. 9. Gas chromatography-mass spectrometry (GC-MS) analysis for the identification of propene. Chromatograms for (a) standard gas containing propene and for (b) the results of electrochemically dehydrogenating propane to propene. Corresponding mass spectrums of (c) standard gas containing propene and (d) the results of electrochemically dehydrogenating propane to propene. Electrochemical propane dehydrogenation for the resulting data in (b) and (d) was achieved by using a Pt electrocatalyst, 0.1 M LiOH electrolyte, an adsorption potential of 0.3 V vs. the reversible hydrogen electrode (RHE), and a desorption potential of 0.05 V vs. RHE.

[0035] FIG. 10. Resulting product distribution after electrochemical propane dehydrogenation at various adsorption potentials (E_{ads}). Electrochemical propane dehydrogenation for the resulting data was achieved by using a Pt electrocatalyst, 0.1 M LiOH electrolyte, and a desorption potential of 0.05 V vs. RHE.

[0036] FIG. 11. A schematic diagram illustrating that desorption at different pH changes selectivity for alkane vs alkene: (a) potential profile; (b) desorption under acid; and (c) desorption under base.

[0037] FIG. 12. Propene selectivity upon reductive desorption with electrolytes having pH values of 0 and 3.

[0038] FIG. 13. A schematic diagram that illustrates displacement of alkyl adsorbates via competitive adsorption.

[0039] FIG. 14. A schematic diagram that illustrates oxidative removal of adsorbates.

[0040] FIG. 15. A graph depicting results of running the method in 0.1 M sodium perchlorate ($NaClO_4$)+0.001 M $HClO_4$. The n-butane was adsorbed at 0.3 V vs RHE, followed by desorption at 0.05 V vs RHE. The results show that replacing protons with Na^+ cations enhanced the yield toward 1-butene production.

DETAILED DESCRIPTION

[0041] Disclosed herein are methods of dehydrogenating a chemical reactant to yield dehydrogenated product.

[0042] Unless the context dictates otherwise, the general terms “chemical reactant” and “dehydrogenated product” (as well as corresponding terms designating adsorbed forms thereof such as “adsorbed chemical reactant” and “adsorbed chemical product”) can each broadly encompass one or more classes of chemical or compound, one or more species of chemical or compound, and/or one or more individual molecules. “Species” in this context refers to a single individual molecule or a collection of individual molecules having the same molecular formula and connectivity of atoms. “Class” in this context refers to a single species or a collection of more than one species, the latter being defined at any of a variety of levels of generality (e.g., C_2 - C_{12} linear, branched, or cyclic alkanes; C_3 - C_6 linear, branched, or cyclic alkanes; C_2 - C_{12} linear alkanes; C_3 - C_6 alkanes; etc.).

[0043] The chemical reactant preferably comprises one or more C—H bonds.

[0044] In some versions, the chemical reactant comprises a hydrocarbon. The hydrocarbon can be linear, branched, or cyclic and can be saturated or unsaturated. In some versions, the hydrocarbon is a C_2 - C_{12} hydrocarbon, such as a C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , C_{11} , or C_{12} hydrocarbon or a hydrocarbon having a carbon number within a range between any two of the foregoing carbon numbers. In some versions, the chemical reactant comprises an alkane. The alkane can be linear, branched, or cyclic. In some versions, the alkane is a C_2 - C_{12} alkane, such as a C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , or C_{12} alkane or an alkane having a carbon number with a range between any two of the foregoing carbon numbers. Exemplary alkanes include ethane, propane, butane, pentane, octane.

[0045] In some versions, the chemical reactant comprises a polymer whose backbone comprises carbon atoms. The polymers may be obtained from recycled plastic or waste plastic. Exemplary polymers include addition polymers and condensation polymers. Exemplary addition polymers and condensation polymers include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinyl chloride, polypropylene, and polystyrene.

[0046] The methods disclosed and claimed herein can comprise a step of adsorbing the chemical reactant to the electrode. In methods in which the chemical reactant comprises more than one individual molecule, the adsorbing comprises adsorbing at least a portion of the chemical reactant to the electrode. The adsorption can be achieved by applying an adsorption potential to the electrode. As used herein, “adsorption potential” refers to an electrical potential applied to the electrode that, at minimum, results in adsorption of the chemical reactant to the electrode. In some versions, the adsorption potential is greater or less than the potential of zero charge of the electrode. In various versions, the adsorption potential is from about -1.0 V to about 1.5 V relative to a standard hydrogen electrode, such as about 0.1 V, about 0.2 V, about 0.3 V, about 0.4 V, about 0.5 V, about 0.6 V, about 0.7 V, about 0.8 V, about 0.9 V, or about 1 V, or a value within a range between and encompassing any two of the foregoing values.

[0047] In one version, the methods disclosed herein comprise a step of dehydrogenating the adsorbed chemical reactant. In methods in which the adsorbed chemical reactant comprises more than one individual molecule, the dehydrogenating comprises dehydrogenating at least a portion of the adsorbed chemical reactant. The dehydrogenation can be achieved by applying a dehydrogenation potential to the electrode for a time effective to break at least one of the C—H bonds in the adsorbed chemical reactant to yield adsorbed dehydrogenated product. As used herein, “dehydrogenation potential” refers to an electrical potential applied to the electrode that, at minimum, maintains adsorption of the chemical reactant to the electrode and causes dehydrogenation of C—H bonds in adsorbed chemical reactant. In some versions, the dehydrogenation potential is greater or less than the potential of zero charge of the electrode. In various versions, the dehydrogenation potential is from about 0.1 V to about 1.5 V relative to a standard hydrogen electrode, such as about 0.1 V, about 0.2 V, about 0.3 V, about 0.4 V, about 0.5 V, about 0.6 V, about 0.7 V, about 0.8 V, about 0.9 V, or about 1 V, or a value within a range between and encompassing any two of the foregoing values.

[0048] One aspect of the method is directed to dehydrogenating the chemical reactant without “cracking” it, that is, without breaking any of the C—C bonds in the reactant(s).

[0049] Accordingly, in various versions, the dehydrogenating breaks at least one of the C—H bonds without breaking any of the C—C bonds in at least 0.0001% by number, at least 0.0005% by number, at least 0.001% by number, at least 0.005% by number, at least 0.01% by number, at least 0.05% by number, at least 0.1% by number, at least 0.5% by number, at least 1% by number, at least 2% by number, at least 3% by number, at least 4% by number, at least 5% by number, at least 6% by number, at least 7% by number, at least 8% by number, at least 9% by number, at least 10% by number, at least 15% by number, at least 20% by number, at least 25% by number, at least 30% by number, at least 35% by number, at least 40% by number, at least 45% by number, or at least 50% by number of the at least one species of adsorbed chemical reactant. In various versions, the dehydrogenating breaks at least one of the C—H bonds without breaking any of the C—C bonds in up to 0.0005% by number, up to 0.001% by number, up to 0.005% by number, up to 0.01% by number, up to 0.05% by number, up to 0.1% by number, up to 0.5% by number, up to 1% by number, up to 2% by number, up to 3% by number, up to 4% by number, up to 5% by number, up to 6% by number, up to 7% by number, up to 8% by number, up to 9% by number, up to 10% by number, up to 15% by number, up to 20% by number, up to 25% by number, up to 30% by number, up to 35% by number, up to 40% by number, up to 45% by number, or up to 50% by number of at least one species of the adsorbed chemical reactant. The species in some such versions can comprise a C_2 - C_{12} hydrocarbon species, such as a C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , or C_{12} hydrocarbon species or a hydrocarbon species having a carbon number within a range between any two of the foregoing carbon numbers. An exemplary species is a C_4 hydrocarbon species.

[0050] In some versions, the dehydrogenation potential is other than a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in at least one species. Similarly, in various versions, the dehydrogenation potential is not within ± 0.001 V, ± 0.002 V, ± 0.003 V, ± 0.004 V, ± 0.005 V, ± 0.006 V, ± 0.007 V, ± 0.008 V, ± 0.009 V, ± 0.01 V, ± 0.02 V, ± 0.03 V, ± 0.04 V, ± 0.05 V, ± 0.06 V, ± 0.07 V, ± 0.08 V, ± 0.09 V, ± 0.1 V, ± 0.15 V, ± 2 V, or ± 2.5 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in the at least one species. The species in some such versions can comprise a C_2 - C_{12} hydrocarbon species, such as a C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , or C_{12} hydrocarbon species or a hydrocarbon species having a carbon number within a range between any two of the foregoing carbon numbers. An exemplary species is a C_4 hydrocarbon species.

[0051] In various versions, the dehydrogenation potential is a potential within ± 0.001 V, ± 0.002 V, ± 0.003 V, ± 0.004 V, ± 0.005 V, ± 0.006 V, ± 0.007 V, ± 0.008 V, ± 0.009 V, ± 0.01 V, ± 0.02 V, ± 0.03 V, ± 0.04 V, ± 0.05 V, ± 0.06 V, ± 0.07 V, ± 0.08 V, ± 0.09 V, ± 0.1 V, ± 0.15 V, ± 2 V, ± 2.5 V, ± 3.5 V, ± 4 V, ± 4.5 V, ± 5 V, ± 5.5 V, or ± 6 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species. In some versions, the dehydrogenation potential

is a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species. The species in some such versions can comprise a C₂–C₁₂ hydrocarbon species, such as a C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, or C₁₂ hydrocarbon species or a hydrocarbon species having a carbon number within a range between any two of the foregoing carbon numbers. An exemplary species is a C₄ hydrocarbon species.

[0052] Any of the characteristics described herein for the dehydrogenation potential can apply to the adsorption potential. In some versions, the adsorption potential and the dehydrogenation potential are within the same defined range. In various versions, The adsorption potential and the dehydrogenation potential are within ± 0.001 V, ± 0.002 V, ± 0.003 V, ± 0.004 V, ± 0.005 V, ± 0.006 V, ± 0.007 V, ± 0.008 V, ± 0.009 V, ± 0.01 V, ± 0.02 V, ± 0.03 V, ± 0.04 V, ± 0.05 V, ± 0.06 V, ± 0.07 V, ± 0.08 V, ± 0.09 V, ± 0.1 V, ± 0.15 V, ± 2 V, ± 2.5 V, ± 3.5 V, ± 4 V, ± 4.5 V, ± 5 V, ± 5.5 V, or ± 6 V relative to a standard hydrogen electrode of each other. In some versions, the adsorption potential and the dehydrogenation potential are the same, such that applying the adsorption potential in the adsorbing step and applying the dehydrogenation potential in the dehydrogenating steps are performed by initially applying the electrode potential to a particular potential to induce adsorption in the adsorbing step and maintaining that potential to maintain adsorption while inducing dehydrogenation in the dehydrogenation step.

[0053] The methods disclosed herein can comprise a step of desorbing the adsorbed dehydrogenated product from the electrode. In methods in which the chemical reactant comprises more than one individual molecule, the desorbing comprises desorbing at least a portion of the adsorbed dehydrogenated product from the electrode. The desorption can be achieved by applying a desorption potential to the electrode to thereby yield a desorbed dehydrogenated product. As used herein, “desorption potential” refers to an electrical potential applied to the electrode that, at minimum, results in desorption of the chemical reactant from the electrode. The desorption potential is preferably lower (e.g., less positive) than either or both of the adsorption potential and the dehydrogenation potential. In some versions, the desorption potential is within an underpotential deposition range for hydrogen (H_{UPD}) on the electrode. In some versions, the desorption potential is less than 0.1 V, less than 0.09 V, less than 0.08 V, less than 0.07 V, less than 0.06 V, less than 0.05 V, less than 0.04 V, less than 0.03 V, less than 0.02 V, less than 0.01 V, less than 0.001 V, less than 0.009 V, less than 0.008 V, less than 0.007 V, less than 0.006 V, less than 0.005 V, less than 0.004 V, less than 0.003 V, less than 0.002 V, less than 0.0001 V relative to a standard hydrogen electrode.

[0054] The dehydrogenated product can comprise any dehydrogenated form of any chemical reactant described herein. In some versions, the dehydrogenated product is an unsaturated hydrocarbon. The unsaturated hydrocarbon can be linear, branched, or cyclic. In some versions, the unsaturated hydrocarbon is a C₂–C₁₂ unsaturated hydrocarbon, such as a C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ unsaturated hydrocarbon or an unsaturated hydrocarbon having a carbon number within a range between any two of the foregoing carbon numbers. In some versions, the chemical reactant comprises an alkene. The alkene can be linear,

branched, or cyclic. In some versions, the alkene is a C₂–C₁₂ alkene, such as a C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, or C₁₂ alkene or an alkene having a carbon number with a range between any two of the foregoing carbon numbers. Exemplary alkenes include ethylene, propylene, butylene (e.g., 1-butene, cis-2-butene, trans-2-butene, isobutene), pentene (e.g., pent-1-ene, cis-pent-2-ene, trans-pent-2-ene), octene (including any isomer). In some versions, the dehydrogenated product comprises a dehydrogenated form of any polymer described herein.

[0055] The methods can comprise a step of introducing the chemical reactant to an electrode of an electrochemical cell. The introducing can be performed in such a manner that the chemical reactant can come into contact with the electrode. Depending on the format, the chemical reactant can be introduced to the electrode in a liquid phase, such as in a phase with an electrolyte, or in other phases, such as a gas phase.

[0056] In some versions, for example, the methods are conducted in a flow cell. See, e.g., FIG. 2B. The flow cell can be configured for the chemical reactant being introduced to one face of the electrode and the electrolyte to be disposed on the opposite face. The chemical reactant can be introduced to the electrode within a fluid (e.g., liquid or gas) feedstock to the first face with the potentials being induced via the electrolyte on the opposite face. In versions in which the chemical reactant is introduced in the gas phase, the electrode can comprise a gas diffusion electrode.

[0057] Regardless of the format, the electrode can comprise one or more metals. Exemplary metals include but are not limited to Pt, Au, Ag, Cu, Fe, Rh, Ni, Pd, Ir, Co, V, Cr, Sn, Ti, W, or any alloys, sulfides, nitrides, oxides, or carbides thereof. Exemplary alloys include but are not limited to CoMo sulfide, NiMo sulfide, Mn oxide/SnO₂, Co oxide/SnO₂, MoV mixed metal oxide (MMO), TeNb MMO, and W-doped MoVMn.

[0058] In preferred versions, the electrolyte may comprise an acid. Any acidic electrolyte, without limitation, can be used. The electrolyte can comprise any strong acid. Exemplary strong acids include HCl, HBr, HI, H₂SO₄, HNO₃, HClO₃, HClO₄, or any combination of these. Alternatively, the electrolyte may comprise an acid. Any basic electrolyte, without limitation, can be used. Exemplary strong bases include LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂, or any combination of these.

[0059] In some versions, any one or more steps of the methods described herein (e.g., the introducing, the adsorbing, the dehydrogenating, and/or the desorbing, in any combination) are performed at a temperature of 100.0° C. or below. In some versions, the steps are performed at a temperature from about 0.0° C. to about 100.0° C., such as from about 4° C. to about 50° C., from about 15° C. to about 30° C., or from about 15° C. to about 25° C. In some versions, the steps are performed at ambient temperature, without an externally applied source of heat other than the applied electrical potentials. The ambient temperature can be any of the foregoing temperatures.

[0060] In some versions, any one or more steps of the methods described herein (e.g., the introducing, the adsorbing, the dehydrogenating, and/or the desorbing, in any combination) are performed at ambient pressure. In versions, the ambient pressure is between 0.8 and 1.2 atm.

[0061] In other versions of the method, electrolyte components that strongly bind to the electrode surface, such as

I⁻, Cl⁻, Cu²⁺, Ce²⁺, and/or CN⁻ may optionally be added to the electrolyte formulation. In additional versions, protons in the electrolyte may be replaced with one or more cations selected from the group consisting of alkali metal cations (e.g., Li⁺, Na⁺, K⁺) and multivalent cations (e.g., Cu²⁺, Ce²⁺), thereby increasing the pH of the electrolyte. The presence of these ions may further enhance the driving force for releasing dehydrogenated compounds. See Example 3 in the Example Section. The pH may also be increased independently of adding additional electrolyte species.

[0062] Unless specified otherwise, all potentials herein are reported vs. a standard hydrogen electrode (“SHE”). Voltages may also be reported vs. a reversible hydrogen electrode (“RHE”). SHE voltages can be converted to RHE voltages as a function of pH using the following formula: Energy vs. RHE Voltage=Energy vs. SHE Voltage+(0.059 V*pH). Thus, in the specific case of a pH 0 electrolyte, E vs RHE (V)=E vs SHE (V)+(0.059 V*0), with the outcome RHE Voltage=SHE Voltage. Therefore, in pH 0 electrolyte, the values for SHE and RHE are identical. However, this only holds in pH 0 electrolyte. By way of a non-limiting example, in a pH 13 electrolyte, the following exemplary parameters may be used for alkane adsorption and desorption:

[0063] Adsorb: 0.5 V vs RHE

[0064] Desorb: 0.05 V vs RHE

[0065] Using the above equation, these two values convert to Adsorb at -0.267 V vs SHE and desorb at -0.717 V vs SHE.

[0066] As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the content clearly dictates otherwise.

[0067] As used herein, the term “or” is an inclusive “or” operator and is equivalent to the term “and/or” unless the context clearly dictates otherwise.

[0068] Numerical ranges as used herein are intended to include every number and subset of numbers contained within that range, whether specifically disclosed or not. Further, these numerical ranges should be construed as providing support for a claim directed to any number or subset of numbers in that range. For example, a disclosure of from 1 to 10 should be construed as supporting a range of from 2 to 8, from 3 to 7, from 5 to 6, from 1 to 9, from 3.6 to 4.6, from 3.5 to 9.9, and so forth.

[0069] All patents, patent publications, and peer-reviewed publications (i.e., “references”) cited herein are expressly incorporated by reference to the same extent as if each individual reference were specifically and individually indicated as being incorporated by reference. In case of conflict between the present disclosure and the incorporated references, the present disclosure controls.

[0070] The elements and method steps described herein can be used in any combination whether explicitly described or not.

[0071] All combinations of method steps as used herein can be performed in any order, unless otherwise specified or clearly implied to the contrary by the context in which the referenced combination is made.

[0072] The method disclosed herein can comprise, consist essentially of, or consist of the essential elements and steps described herein, as well as any additional or optional ingredients, components, or limitations described herein or otherwise useful in the field of electrochemistry. The dis-

closure provided herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

[0073] It is understood that the methods disclosed are not confined to the particular construction and arrangement of parts and steps herein illustrated and described, but embrace all modified and equivalent forms thereof as come within the scope of the claims.

EXAMPLES

Example 1: Dehydrogenation of n-butane

Summary

[0074] An exemplary electrochemical method for the dehydrogenation of alkanes (such as n-butane to produce olefins (such as C₄ olefins (butenes)) at ambient temperature and atmospheric pressure is provided below. (As used herein, the term “alkane” is defined to mean ethane and all linear, branched, and cyclic alkanes having three or more carbon atoms; C₂ to C₁₂ alkanes are generally preferred, although not required, for use as reactants in the method.) This process employs a dynamically controlled electrode potential in an electrochemical cell equipped with a gas diffusion electrode coated with a catalyst (e.g., platinum or palladium catalysts). By modulating the electrode potential between oxidative and reductive states, the method efficiently facilitates the adsorption, dehydrogenation, and desorption of alkanes (such as n-butane) and its intermediates. The method overcomes the limitations of traditional high-temperature processes, offering a sustainable and energy-efficient approach to olefin production without the need for external heating or pressurization.

Background

[0075] The dehydrogenation of n-butane produces butenes and hydrogen. Thermodynamically, this reaction is endothermic, and the yield of butenes is limited by equilibrium constraints. Consequently, high temperatures and low pressures are often employed in industrial settings to favor product formation. However, elevated temperatures can adversely affect the adsorption of reactants and intermediates by decreasing their binding energies. This trade-off between binding energy and catalytic activity is described by the Sabatier principle, which states that an optimal catalyst should have a moderate binding affinity for the relevant adsorbed intermediates along the desired reaction pathway. Therefore, future n-butane dehydrogenation processes should aim to reach the Sabatier optimum. However, achieving this optimal condition with a given catalyst is challenging under steady-state operating conditions, such as constant temperature and pressure.

[0076] Recent analyses have shown that the static Sabatier maximum can be overcome by dynamically altering the properties of the catalyst or the operating conditions. Specifically, in the mechanism of direct n-butane dehydrogenation, a strong-binding condition facilitates n-butane adsorption and surface dehydrogenation, leading to the accumulation of olefin intermediates on the catalyst surface. Before the surface coverage becomes excessive and time is “wasted” under this condition, the catalyst is transiently shifted to a weak-binding state, which promotes the desorption of the accumulated olefin intermediates into the gas phase as products. However, a significant challenge for

dynamic dehydrogenation catalysis is its experimental implementation. For direct dehydrogenation of butane based on thermal catalysis (e.g., the CATADIENE® process), rapidly achieving transitions in reaction temperature or pressure is nearly impossible.

[0077] The present examples show an electrochemical method for n-butane dehydrogenation in an aqueous electrolyte under ambient temperature and pressure. Unlike the challenges associated with rapidly adjusting temperature and pressure, controlling the electrode potential offers greater flexibility. By leveraging a dependence of neutral molecule adsorption on the electrode's potential of zero charge and a volcano-type relationship between adsorption coverage and applied potentials, we selected two distinct potentials on either side of the peak to decouple n-butane dehydrogenation into two steps: oxidative conversion and reductive desorption. Adsorption and conversion occur at a more positive potential, while desorption takes place at a less positive potential (FIG. 1). These steps enable the dehydrogenation reaction to proceed efficiently under ambient conditions.

Methods

[0078] To enable rapid potential switching and efficient mass transfer, we employed a gas diffusion electrode (GDE) (FIG. 2A) and a flow cell (FIG. 2B) for the electrochemical conversion of n-butane. A 100 nm layer of platinum (Pt) and palladium (Pd) was sputtered onto the surface of hydrophobic carbon paper (H15C13, Freudenberg) to serve as the electrodes. During testing, the catalyst side faced the electrolyte (1 M perchloric acid, HClO_4 , pH=0), while the back side of the electrode was exposed to the gas phase—either pure n-butane flow or pure argon flow. The porous and hydrophobic nature of the carbon paper substrate facilitated the formation of a three-phase interface. In this configuration, the reaction substrate does not need to dissolve in the electrolyte and diffuse through the liquid phase to reach the electrode surface. Instead, n-butane can travel short diffusion distances with high diffusion coefficients, moving directly from the gas phase through the pores of the carbon paper to contact the reaction sites. Furthermore, the gas diffusion electrode allows gaseous products (butenes and other by-products) to diffuse back into the gas phase before nucleating on the surface and blocking active sites. Thus, this device design, combined with potential modulation, may offer a more favorable approach for butane dehydrogenation reactions.

[0079] As previously mentioned, for selecting adsorption potentials, we set the potential intervals around the potential of zero charge of Pt (0.3 V vs. standard hydrogen electrode, SHE) and Pd (0.1 V vs. SHE) to maximize n-butane adsorption. We carefully chose potentials at 0.2 V, 0.3 V, 0.4 V, 0.5 V, and 0.7 V vs. SHE to minimize unwanted oxidation of the adsorbed n-butane or butenes. For the desorption potentials, we selected values of 0.05 V vs. SHE, which is significantly distant from the potential of zero charge. According to the reported cyclic voltammetry curves of Pt and Pd, this desorption potential falls within the underpotential deposition range for hydrogen (HUPD). In this range, HUPD can displace surface adsorbates, promoting product desorption.

[0080] While mass spectrometry offers rapid product analysis and quantification, it struggles to distinguish

between butenes and butanes due to their similar fragmentation patterns. Additionally, it has difficulty differentiating between olefin isomers. Therefore, we employed gas chromatography for product separation. Although online gas chromatography is typically used for real-time product analysis, it requires a continuous flow of substrate gas through the reactor, which dilutes the product concentration. This setup is not ideal for electrochemical butane conversion reactions involving monolayer adsorption. Consequently, we opted for offline gas chromatography instead (FIG. 3). In the examples herein, the system as shown in FIG. 3 was used with the procedure as follows:

[0081] 1. Preparation: The argon gas flow into the reactor gas chamber was controlled at 10 standard cubic centimeters per minute (sccm) using a mass flow controller (MFC, Alicat). The electrode surface was cleaned by performing three cycles of cyclic voltammetry at a scan rate of 10 mV/s over the potential range from -0.1 V to +1.3 V vs. SHE.

[0082] 2. Introduction of n-Butane: After cleaning, the potential was set to the open-circuit potential, and n-butane gas was introduced into the reactor gas chamber at a flow rate of 10 sccm by switching a three-way valve. The system was allowed to stabilize at the open-circuit potential for 5 minutes. (The open circuit potential is the electrode potential at zero current density; no current is running through the electrodes. Beginning a run at the open-circuit potential displaces any argon left in the reaction chamber and ensures that the reaction chamber is filled with reactant prior to beginning the reaction.)

[0083] 3. Adsorption and Conversion: The adsorption potential was applied and maintained for 30 minutes. During the first 15 minutes of this period, 10 sccm of n-butane continuously flowed through the reactor gas chamber and was vented. In the following 12 minutes, 60 sccm of argon was introduced into the gas chamber to purge any residual n-butane.

[0084] 4. Desorption: In the final 3 minutes of the adsorption stage, connect a gas-tight syringe (6 mL, equipped with a Luer-lock fitting) to the three-way valve at the reactor gas outlet, while keeping the syringe-valve connection closed. During this period, the effluent gas from the reactor is vented directly through the valve. The MFC is set to flow-control mode with a target flow rate of 1 sccm. When the potential is switched to the desorption potential, quickly switch the three-way valve to direct the gas products into the syringe. The syringe plunger is then gradually pushed outward, ensuring complete collection of all desorbed products within approximately 5 minutes.

[0085] 5. Sample Injection: The syringe was then disconnected from the reactor. Using a needle, the entire sample in the syringe was fully injected into the column (12'x1/8" stainless steel HayeSep D packed column) through the on-column injection port.

[0086] 6. Post-Desorption Cleaning: After holding the desorption potential for an additional 5 minutes, the electrode surface was cleaned via cyclic voltammetry (the parameters are the same as in Step 1.) to oxidize any species that had not desorbed, converting them into CO_2 . During this process, a gas-tight syringe (6 mL) remained connected to the reactor outlet, and the MFC was kept in flow-controlled mode (set to 1 sccm),

ensuring that all oxidation products were collected for chromatographic quantification.

[0087] This procedure allowed for precise collection and analysis of the desorption products, facilitating an accurate assessment of the electrochemical n-butane conversion process.

Results

[0088] Based on the gas chromatogram (FIG. 4), when the Pt electrode was used, the desorption products included not only butenes but also methane, ethane, ethylene, and propane. The presence of these products was further confirmed by additional gas chromatography-mass spectrometry (GC-MS analysis, FIG. 5). These results indicate that, in addition to n-butane dehydrogenation, C—C bond cleavage occurred on the electrode surface, suggesting that n-butane has a strong adsorption energy on the Pt electrode, leading to deeper cleavage reactions. As the dehydrogenation reaction involves breaking only a single C—H bond, whereas the cleavage reaction requires breaking multiple C—C and C—H bonds, the two reactions likely occur with different barriers. Therefore, we propose that the ratio of cleavage to dehydrogenation reactions can be controlled by adjusting the adsorption potentials. Additionally, the results from post-reaction electrode cleaning showed that only significant amounts of CO₂ were detected (FIG. 6), with no additional olefins or alkanes present. This suggests that the electrode surface was effectively cleaned, and nearly all adsorbates had either desorbed or been oxidized to CO₂.

[0089] Using an established GC testing method, we further investigated the impact of adsorption potential on product distribution. By systematically varying the adsorption potential while keeping the desorption potential constant at 0.05 V vs. SHE, we tracked how the desorption products changed in relation to the adsorption potential (FIG. 7A). Our observed product distribution depended strongly on the potential applied during adsorption. Specifically, 1-butene and propane exhibited a common volcano-shaped trend between yield and adsorption potential, with a maximum at 0.5 V vs SHE. Ethane and ethylene also followed a common volcano-shaped trend, albeit with a peak at 0.3 V vs SHE.

[0090] We further evaluated the n-butane dehydrogenation performance of different electrode materials (FIG. 7B). Observing that the strong adsorption energy (Metal-C adsorption) of n-butane on Pt surfaces leads to deep cracking of n-butane (C—C bond cleavage), we hypothesized that employing materials with weaker butane adsorption energy but still strong hydrogen adsorption energy could inhibit cracking while promoting the dehydrogenation reaction (C—H bond cleavage) of n-butane. Therefore, we used Pd as the electrode material. Under the same adsorption and desorption potentials, we found that the proportion of deep cracking products (methane and ethane) from n-butane on the Pd surface decreased, with propane becoming the main multicarbon alkane product (FIG. 8). Simultaneously, the proportion of 1-butene increased. We anticipate that these methods can be extended to other alloys or even single-atom catalysts to improve the performance of n-butane dehydrogenation under mild conditions.

[0091] To improve the selectivity toward alkene production, we next modified the electrolyte composition. We considered that desorption may involve the displacement of surface adsorbates through the adsorption of *H to the

catalyst (i.e., Hupd). However, the presence of surface *H likely also leads to the hydrogenation of a fraction of the dehydrogenated adsorbates back to saturated alkanes. By increasing the electrolyte pH, we aimed to decrease the proton concentration at the electrode surface, and thereby suppress undesirable hydrogenation during the desorption step. To maintain the ionic strength, we replaced protons with Na⁺ ions and carried out our experiments in 0.1 M sodium perchlorate (NaClO₄)+0.001 M HClO₄. To compensate for the pH change, we maintained the adsorption and desorption potential constant vs the reversible hydrogen electrode (RHE) scale. We adsorbed n-butane at 0.3 V vs RHE, followed by desorption at 0.05 V vs RHE. The results (presented in FIG. 15) show that replacing protons with Na⁺ cations enhanced the yield toward 1-butene production. This indicates that under the conditions of increased pH and increased alkali metal cation concentration, the dehydrogenated intermediates indeed have a higher propensity to desorb in the form of unsaturated products. Interestingly, however, we also observed an increase in propane production, but no longer detectable ethylene or ethane. This change in product distribution may be associated with a change to the bonding mode of n-butane fragments under the changed electrolyte conditions.

Discussion

[0092] Several techniques for electrochemical alkane dehydrogenation at high temperatures or under mild conditions already exist, but they have certain limitations.

[0093] High-temperature electrochemical dehydrogenation of alkanes is primarily achieved using solid oxide electrolytic cells (SOECs), where the electrolytes are often stabilized zirconias such as calcium-stabilized zirconia (CSZ), magnesium-stabilized zirconia (MSZ), scandium-stabilized zirconia (ScSZ), titanium-stabilized zirconia (TiSZ), and yttrium-stabilized zirconia (YSZ), as well as samarium-doped ceria (SDC) and perovskite materials. In these systems, the charge carriers are either oxygen ions (O²⁻) or protons, and to maintain high electrical conductivity, operating temperatures typically exceed 500° C. Consequently, these technologies cannot operate at ambient temperatures, leading to increased carbon emissions. Moreover, such high temperatures accelerate coking on the electrode surface. Additionally, hydrogen is often co-fed to facilitate the desorption of the produced olefins, which, along with the energy costs associated with maintaining high temperatures and the expense of hydrogen feedstock, increases production costs. In contrast, the techniques of the present disclosure do not require high temperatures and can be performed at room temperature. The technology of the present disclosure can employ a liquid aqueous electrolyte to facilitate the desorption of olefins by generating HUPD under electrochemical conditions, eliminating the need to co-feed hydrogen. Therefore, it offers advantages over solid oxide electrolytic cells.

[0094] Alkane dehydrogenation using homogeneous transition metal molecular catalysts can significantly reduce the reaction temperature, with common reaction temperatures around 120° C. Pincer-ligated iridium complexes are among the most commonly used catalysts for this purpose. However, in such systems, continuous removal of the by-product hydrogen is necessary, often achieved by refluxing, which requires additional energy input. Furthermore, due to the low concentration of hydrogen, the removal process tends to

be time-consuming, significantly increasing the overall reaction time. Introducing a sacrificial olefinic hydrogen acceptor is another common method for hydrogen expulsion but adds to the cost and complicates catalyst separation and recovery. The technology of the disclosure can utilize a heterogeneous electrode with easy catalyst recovery through post-reaction cyclic voltammetry cleaning. By rapidly switching the potential, dehydrogenation can be achieved while keeping the intermediate product bound to the catalyst surface, which means no hydrogen is generated during the dehydrogenation process.

[0095] Recently, an alkane dehydrogenation process operating at ambient temperature and pressure has been demonstrated using copper particles as catalysts in an acidic electrolyte. In this method, a Cu_2O layer forms on the surface of the copper particles and serves as the catalyst. However, Cu_2O readily dissolves in the acidic solution to form Cu^{2+} ions, leading to a loss of catalytic activity. To extend the reaction time, additional oxygen is often introduced to re-oxidize the copper particles. Eventually, all the copper particles dissolve into the acidic electrolyte as Cu^{2+} ions and cannot be regenerated. In contrast, the technology of the disclosure allows for catalyst recycling without the need for additional oxygen feed. We consume the hydrogen produced during the dehydrogenation reaction solely through oxidative polarization, enhancing both the efficiency and sustainability of the process.

[0096] In summary, the technology of the disclosure relies solely on potential switching to achieve both dehydrogenation and product desorption—that is, oxidative potential for adsorption and dehydrogenation, and reductive potential for desorption—making it distinct from previous electrochemical technologies or dehydrogenation processes under mild conditions. Notably, the approach as described herein does not require the introduction of additional gases such as hydrogen or oxygen, making the process more efficient and convenient. Furthermore, the methods of the disclosure offer significant advantages in catalyst recovery and regeneration. Therefore, the technology of the disclosure presents considerable benefits and practical applicability.

[0097] The technology of the disclosure can leverage shale gas to produce olefins, using electricity generated from renewable sources like solar power, thereby minimizing carbon emissions. The reactors can operate at ambient temperature and pressure without the need for complex pressure or temperature control components, making them suitable for compact installations. The units can be solar-powered and integrated directly into alkane gas pipelines for dehydrogenation reactions.

Example 2: Dehydrogenation of Propane

Methods

[0098] To enable rapid potential switching and efficient mass transfer, we employed a gas diffusion electrode (GDE) for the electrochemical conversion of propane. A 100 nm layer of platinum (Pt) was sputtered onto the surface of hydrophobic carbon paper (H15C13, Freudenberg) to serve as the electrode. During testing, the catalyst side faced the electrolyte (0.1 M LiOH, pH=13), while the back side of the electrode was exposed to the gas phase—either pure propane flow or pure argon flow. The porous and hydrophobic nature of the carbon paper substrate facilitated the formation of a three-phase interface. In this configuration, the reaction

substrate does not need to dissolve in the electrolyte and diffuse through the liquid phase to reach the electrode surface. Instead, propane can travel short diffusion distances with high diffusion coefficients, moving directly from the gas phase through the pores of the carbon paper to contact the reaction sites. Furthermore, the gas diffusion electrode allows gaseous products (propene and other by-products) to diffuse back into the gas phase before nucleating on the surface and blocking active sites. Thus, this device design, combined with potential modulation, may offer a more favorable approach for propane dehydrogenation reactions.

[0099] We carefully chose adsorption potentials at 0.3 V, 0.5 V, and 0.7 V vs. RHE to minimize unwanted oxidation of the adsorbed propane or propene. For the desorption potentials, we selected values of 0.05 V vs. RHE. According to the reported cyclic voltammetry curves of Pt, this desorption potential falls within the underpotential deposition range for hydrogen (H_{UPD}). In this range, H_{UPD} can displace surface adsorbates, promoting product desorption.

[0100] While mass spectrometry offers rapid product analysis and quantification, it struggles to distinguish between propane and propene due to their similar fragmentation patterns. Therefore, we employed gas chromatography (GC) for product separation. Although online gas chromatography is typically used for real-time product analysis, it requires a continuous flow of substrate gas through the reactor, which dilutes the product concentration. This setup is not ideal for electrochemical propane conversion reactions involving monolayer adsorption. Consequently, we opted for offline gas chromatography instead.

[0101] In the examples herein, a system similar to that shown in FIG. 3 (except that propane served as the reactant instead of n-butane) was used with the procedure as follows:

[0102] 1. Preparation: The argon gas flow into the reactor gas chamber was controlled at 30 standard cubic centimeters per minute (sccm) using a mass flow controller (MFC, Alicat). The electrode surface was first cleaned by applying a constant potential of +2.07 V vs. RHE. Following this, the electrode surface was further cleaned by performing three cycles of cyclic voltammetry between +0.05 V and +1.3 V vs. RHE at a scan rate of 20 mV/s.

[0103] 2. Introduction of Propane at the adsorption potential: After cleaning, the potential was set to a constant adsorption potential (i.e. 0.3 V, 0.5 V, 0.7 V vs. RHE). For the first five minutes of the potential hold, Ar was continuously flown into the system at 30 sccm. At the five-minute mark, propane gas was introduced into the reactor gas chamber at a flow rate of 30 sccm by switching a three-way valve. After 30 minutes of propane flow at the adsorption potential, propane flow was stopped and replaced with Ar flow at a rate of 30 sccm to purge any residual propane.

[0104] 3. Reductive desorption of products: In the final 60 seconds of the adsorption stage, a gas-tight syringe (3 mL, equipped with a Luer-lock fitting) was connected to the three-way valve at the reactor gas outlet, while keeping the syringe-valve connection closed. During this period, the effluent Ar gas from the reactor is vented directly through the valve. 10 seconds before the end of the adsorption stage, the Ar flow rate was lowered to 1.5 sccm. At the start of the reductive desorption stage, the potential is set to +0.05 V vs. RHE, and the three-way valve is quickly switched to

direct gaseous products from the reactor into the syringe. The syringe plunger is then gradually pushed outward by the flow of Ar, ensuring complete collection of all desorbed products within 1 minute. After product collection, the syringe was closed and the Ar flow rate through the reactor was returned to a rate of 30 sccm. The reductive desorption potential was kept constant for a total of 20 minutes.

[0105] 4. Sample Injection: The syringe was then disconnected from the reactor. Using a needle, the entire sample in the syringe was fully injected into the column of a GC or GC-MS.

[0106] 5. Oxidative desorption of products: After the reductive desorption of products, there still remains surface adsorbates that only desorb through oxidative potentials. In the final 60 seconds of the reductive desorption stage, a gas-tight syringe (3 mL, equipped with a Luer-lock fitting) was connected to the three-way valve at the reactor gas outlet, while keeping the syringe-valve connection closed. During this period, the effluent Ar gas from the reactor is vented directly through the valve. 10 seconds before the end of the adsorption stage, the Ar flow rate was lowered to 1.5 sccm. At the start of the oxidative desorption stage, the potential is set to +1.30 V vs. RHE, and the three-way valve is quickly switched to direct gaseous products from the reactor into the syringe. The syringe plunger is then gradually pushed outward by the flow of Ar, ensuring complete collection of all desorbed products within 1 minute. After product collection, the syringe was closed and the Ar flow rate through the reactor was returned to a rate of 30 sccm.

[0107] 6. Sample Injection: The syringe was then disconnected from the reactor. Using a needle, the entire sample in the syringe was fully injected into the column of a GC through the on-column injection port.

[0108] This procedure allowed for precise collection and analysis of the desorption products, facilitating an accurate assessment of the electrochemical propane conversion process

Results

[0109] Gas chromatography-mass spectrometry (GC-MS) analysis confirmed the formation of propene (FIG. 9).

[0110] FIG. 10 shows product distribution after electrochemical propane dehydrogenation at various adsorption potentials (E_{ads}). The production of methane was not significantly affected by changes in adsorption potential (0.3, 0.5, or 0.7 V vs. RHE). An adsorption potential of 0.5 V vs. RHE resulted in the highest amounts of ethane and propene.

Example 3: Desorption of the Dehydrogenated Products

[0111] In previous studies, the reductive desorption of surface-bound hydrocarbons results in the release of alkanes rather than alkenes (See Lucky et al. "Understanding the interplay between electrocatalytic $C(sp^3)$ - $C(sp^3)$ fragmentation and oxygenation reactions." Nat. Catal., 2024, 7, 1021-1031; Bakshi et al. "Electrocatalytic Scission of Unactivated $C(sp^3)$ - $C(sp^3)$ Bonds through Real-Time Manipulation of Surface-Bound Intermediates." J. Am. Chem. Soc., 2023, 145, 13742-13749). We hypothesize that this is due to the fact that under the strongly acidic conditions, applying a

reductive potential to initiate product desorption will result in a high concentration of hydrogen atoms (H^*) on our catalyst, which recombine with adsorbed hydrocarbon fragments, resulting in the release of hydrogenated products.

[0112] To achieve the desorption of olefins without inducing their hydrogenation, we leveraged interfacial thermodynamics. Applying a reductive potential to an electrode attracts cations and solvent dipoles to the electrode surface. This lowers the chemical potential of adsorbates, in a process governed by the Gibbs-Duhem relation, and thereby displaces adsorbates from the surface without requiring a high concentration of hydrogen atoms. We hypothesized that this can be accomplished under conditions of high pH and in the presence of high concentrations of electrolyte ions (FIG. 11).

[0113] Indeed, we observed that in an experiment involving the adsorption and subsequent desorption of propane from a Pt surface, increasing the electrolyte pH from 0 to 3 led to the appearance of propene as a significant product (FIG. 12). However, it was not known whether olefin generation is related to the pH environment present during adsorption or desorption.

[0114] To gain insight, we studied the desorption of olefins independently from the adsorption and dehydrogenation step. To accomplish this, we adsorbed olefins such as ethylene, propylene, and butene on Pt, Pd, and Rh surfaces at a constant potential. While maintaining the electrode at the adsorption potential, we then exchanged the electrolyte with solutions of varying pH, ionic strength and with different identities of electrolyte ions (e.g. Li^+ , Na^+ , K^+ , as well as multivalent cations). We then applied a progressively more reducing potential and determine the onset of desorption and the selectivity of olefins and hydrogenated compounds as a function of electrolyte and electrode composition. To further enhance the driving force for releasing dehydrogenated compounds, we tested the addition of electrolyte components that strongly bind to the electrode surface, such as I^- , Cl^- , Cu^{2+} , Ce^{2+} , and CN^- (FIG. 13). These compounds have previously been shown to release olefins from Pt and Pd surfaces (Müller et al. "Coadsorption, non-reactive displacement and cathodic desorption of ethene preadsorbed on Pd and Pt electrodes." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1998, 134, 155-164; Müller et al. "Displacement of Ethene and Cyclohexene from Polycrystalline Pt and Pt(110) Electrodes." *J. Phys. Chem. B*, 2000, 104, 24, 5762-5767). These studies will yield optimal conditions for desorbing olefins without inducing their further transformation.

Example 4: Controlling the Degree of Dehydrogenation of Alkane Adsorbates

[0115] To maximize the generation of olefins from n-alkanes, we need to foster conditions which yield the highest possible surface coverage of dehydrogenated alkane fragments. To accomplish this goal, we developed methods to determine the identity of alkyl adsorbates and tune their degree of dehydrogenation through electrolyte and catalyst material modifications. The identity of adsorbates can be determined by their total oxidation to CO_2 . Comparing the number of electrons required for adsorbate oxidation to the number of CO_2 molecules produced (this quantity is termed the "N value") allows us to infer the average number of hydrogen atoms bonded to each carbon atom of an adsorbate (FIG. 14). Using this approach, we can determine the

number of hydrogen atoms attached to alkane adsorbates across a wide range of adsorption potentials, pH, catalyst materials, and electrolyte ion compositions. For example, we hypothesized that more alkaline pH will promote hydrogen atom abstraction from adsorbates, thus leading to more dehydrogenated fragments.

What is claimed is:

1. A method of dehydrogenating a chemical reactant comprising one or more C—H bonds to yield a dehydrogenated product, the method comprising:

introducing the chemical reactant to an electrode of an electrochemical cell;

adsorbing at least a portion of the chemical reactant to the electrode by applying an adsorption potential to the electrode to thereby yield adsorbed chemical reactant comprising one or more C—H bonds;

dehydrogenating at least a portion of the adsorbed chemical reactant by applying a dehydrogenation potential which is the same as or different from the adsorption potential to the electrode for a time effective to break at least one of the C—H bonds in the portion of the adsorbed chemical reactant to thereby yield adsorbed dehydrogenated product; and

desorbing at least a portion of the adsorbed dehydrogenated product from the electrode by applying a desorption potential to the electrode to thereby yield the dehydrogenated product.

2. The method of claim 1, wherein at least one species of the adsorbed chemical reactant comprises one or more C—C bonds.

3. The method of claim 2, wherein the dehydrogenating breaks at least one of the C—H bonds without breaking any of the C—C bonds in at least 0.01% by number of the at least one species of the adsorbed chemical reactant.

4. The method of claim 2, wherein the dehydrogenation potential is other than a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in the at least one species.

5. The method of claim 2, wherein the dehydrogenation potential is not within ± 0.05 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—C bond breakage to C—H bond breakage in the at least one species.

6. The method of claim 2, wherein the dehydrogenation potential is a potential within ± 0.05 V relative to a standard hydrogen electrode of a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species.

7. The method of claim 2, wherein the dehydrogenation potential is a potential that maximizes a ratio of C—H bond breakage to C—C bond breakage in the at least one species.

8. The method of claim 2, wherein the at least one species comprises a C₃ or C₄ hydrocarbon species.

9. The method of claim 1, wherein the adsorption potential and the dehydrogenation potential are greater than a potential of zero charge of the electrode.

10. The method of claim 1, wherein the adsorption potential and the dehydrogenation potential are from about -1.0 V to about 1.5 V relative to a standard hydrogen electrode.

11. The method of claim 1, wherein the desorption potential is less than the adsorption potential and the dehydrogenation potential.

12. The method of claim 1, wherein the desorption potential is less than a potential of zero charge of the electrode.

13. The method of claim 1, wherein the desorption potential is within an underpotential deposition range for hydrogen (H_{UPD}) on the electrode.

14. The method of claim 1, wherein the desorption potential is less than 0.09 V relative to a standard hydrogen electrode (SHE).

15. The method of claim 1, wherein the chemical reactant comprises a saturated hydrocarbon, an unsaturated hydrocarbon, or a polymer whose backbone comprises carbon atoms.

16. The method of claim 1, wherein the chemical reactant comprises a C₂-C₁₂ linear, branched, or cyclic alkane, an addition polymer, a condensation polymer, or any combination thereof.

17. The method of claim 1, wherein the chemical reactant is selected from the group consisting of ethane, and linear, branched, or cyclic propane, butane, pentane, octane, and any combination thereof.

18. The method of claim 1, wherein the dehydrogenated product comprises a C₂-C₁₂ alkene.

19. The method of claim 1, wherein the dehydrogenated product comprises propene and/or butene.

20. The method of claim 1, wherein the adsorbing, the dehydrogenating, and the desorbing are conducted within a flow cell.

21. The method of claim 1, wherein the electrode is a gas diffusion electrode.

22. The method of claim 1, wherein the introducing the chemical reactant comprises introducing the chemical reactant in a gas phase feedstock.

23. The method of claim 1, wherein the electrode comprises one or more metals.

24. The method of claim 1, wherein the electrode comprises one or more metals selected from the group consisting of Pt, Au, Ag, Cu, Fe, Rh, Ni, Pd, Ir, Co, V, Cr, Sn, Ti, W, and alloys, sulfides, nitrides, oxides, and carbides thereof.

25. The method of claim 1, wherein the adsorbing, the dehydrogenating, and the desorbing are conducted at a temperature of from about 15°C to about 30°C .

26. The method of claim 1, wherein the adsorbing, the dehydrogenating, and the desorbing are conducted at a temperature of from about 15°C to about 30°C , and without an externally applied source of heat other than the applied electrical potentials.

27. The method of claim 1, wherein the adsorbing, the dehydrogenating, and the desorbing are conducted at a pressure of from about 0.8 to about 1.2 atm.

28. The method of claim 1, wherein the electrode of the electrochemical cell is in contact with an electrolyte formulation and the electrolyte formulation comprises an ion selected from the group consisting of I^{-} , Cl^{-} , Cu^{2+} , Ce^{2+} , and CN^{-} .

29. The method of claim 1, wherein the electrode of the electrochemical cell is in contact with an electrolyte formulation and the electrolyte formulation comprises a reduced proton concentration relative to an acidic electrolyte.

30. The method of claim 29, wherein at least a portion of the protons in the electrolyte formulation is replaced with one or more cations selected from the group consisting of alkali metal cations and multivalent cations.

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