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(54) **PRETREATING METAL OXIDE CATALYSTS
FOR ALKANE DEHYDROGENATION**

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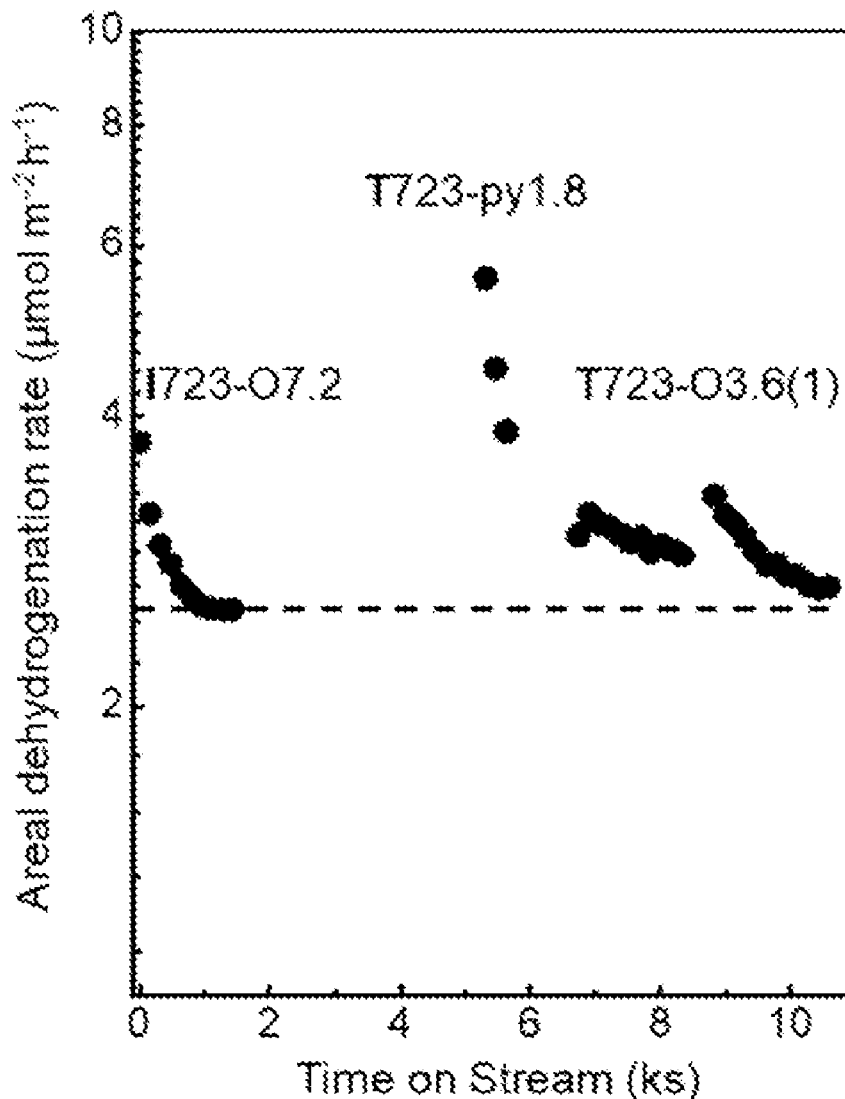
(57) **ABSTRACT**

(22) Filed: **May 18, 2023**

Catalytic dehydrogenation of a light alkane gas on a metal
oxide catalyst is achieved by (a) pretreating the metal oxide
catalyst with dimethylether (DME); and (b) reacting the
alkane gas catalytically on the catalyst in a dehydrogenation
reaction, under conditions wherein the pretreating improves
product yield of the reaction.

Related U.S. Application Data

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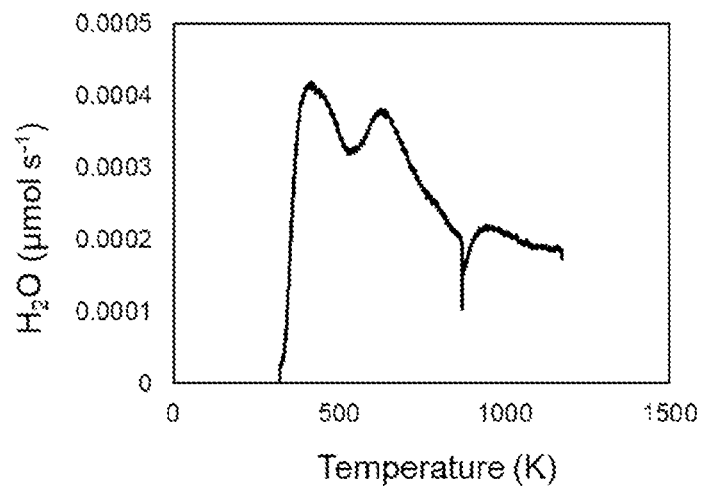


Fig. 1

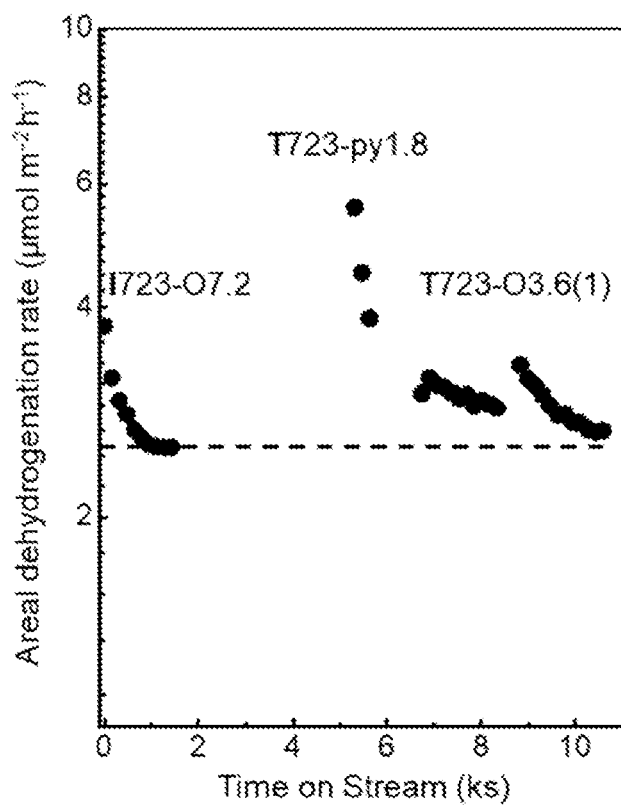


Fig. 2

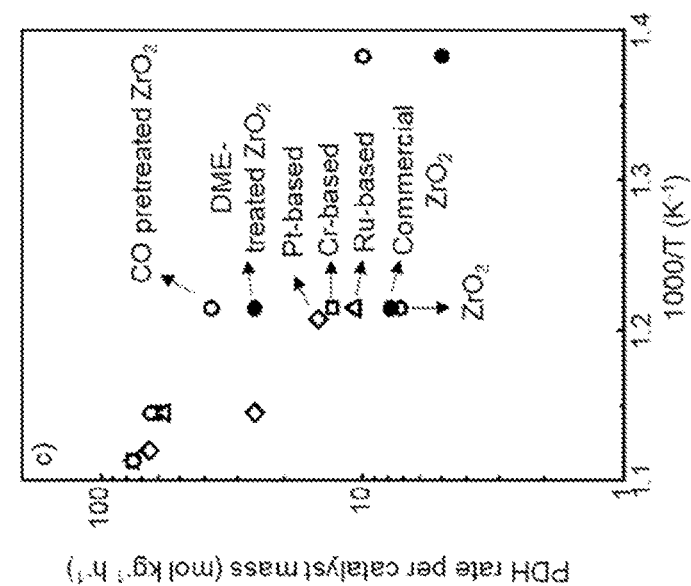


Fig. 3c

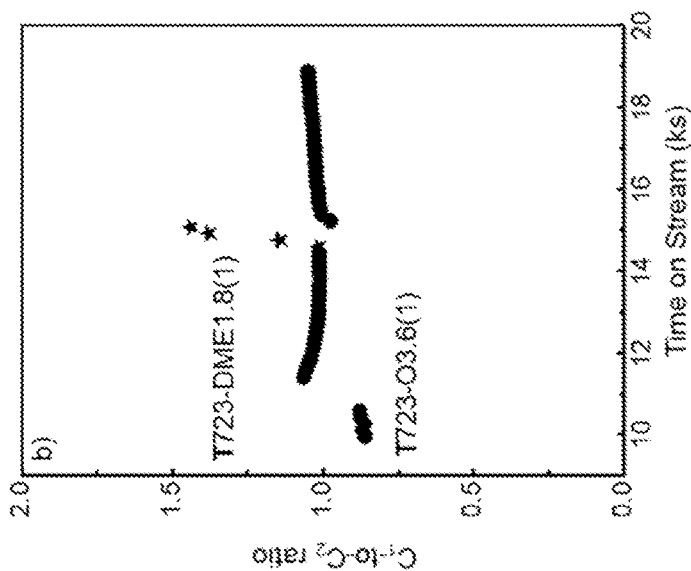


Fig. 3b

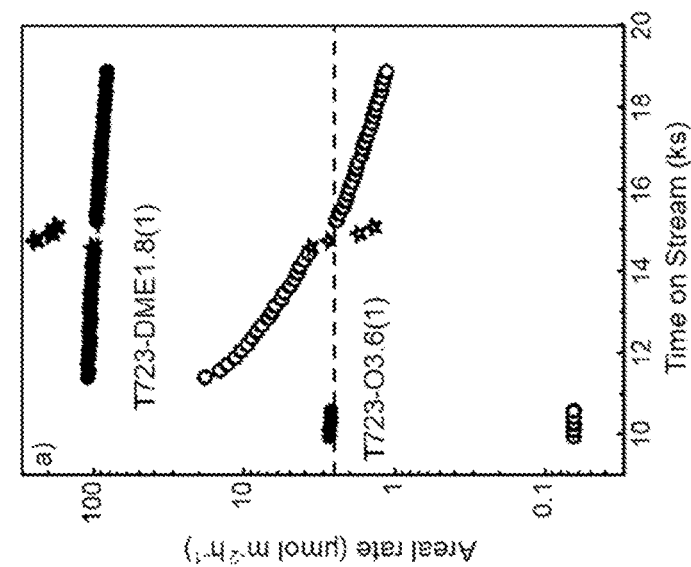


Fig. 3a

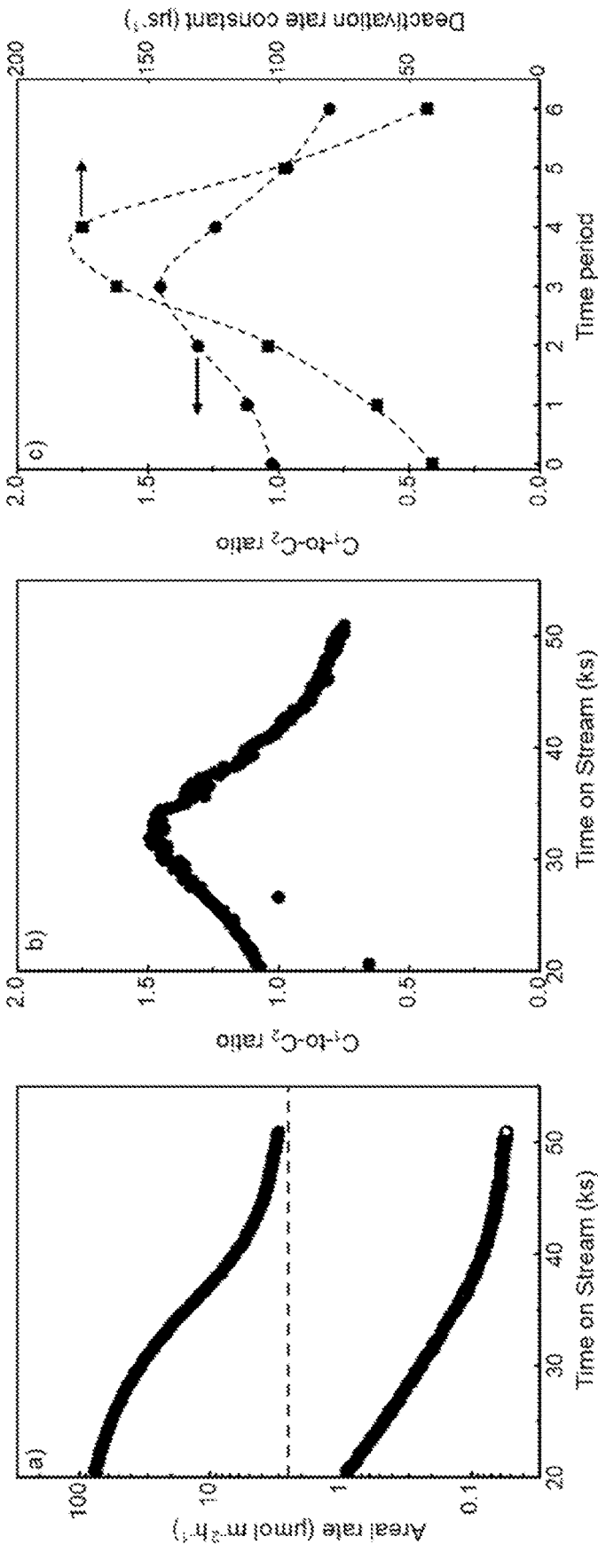


Fig. 4c

Fig. 4b

Fig. 4a

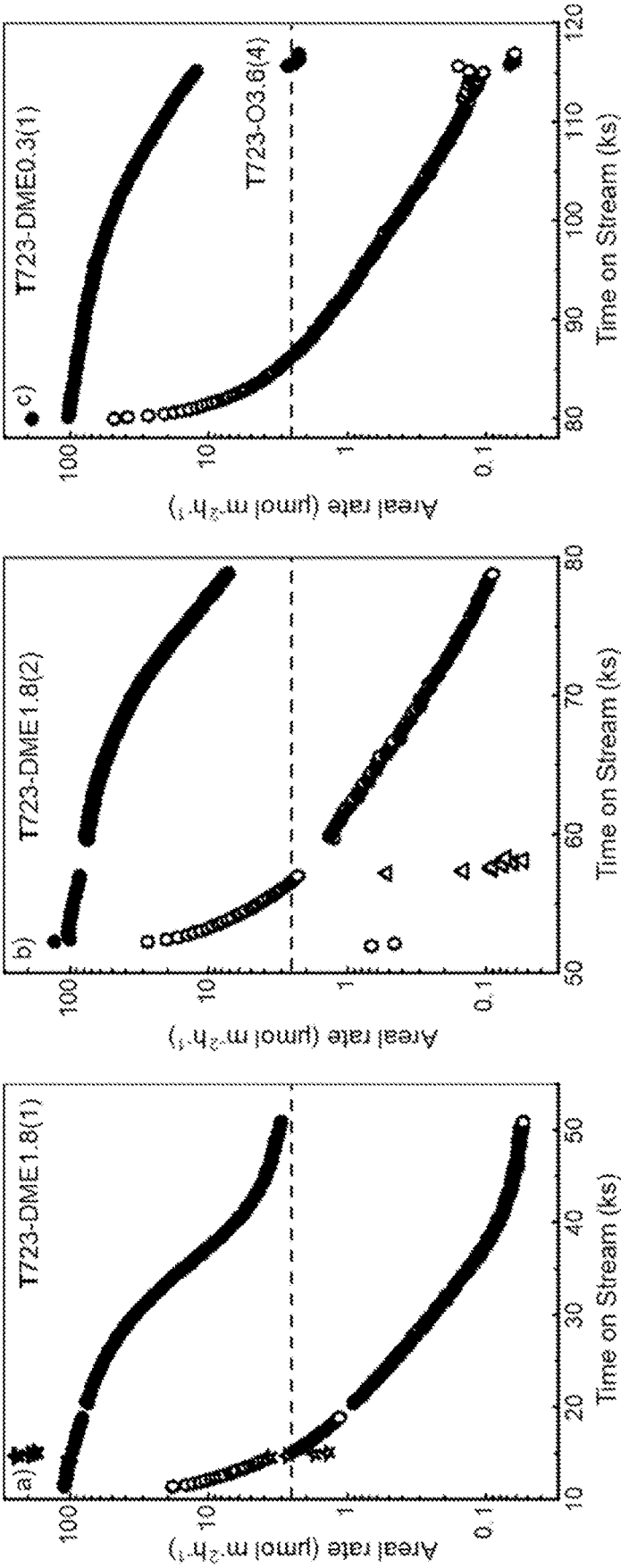


Fig. 5a

Fig. 5b

Fig. 5c

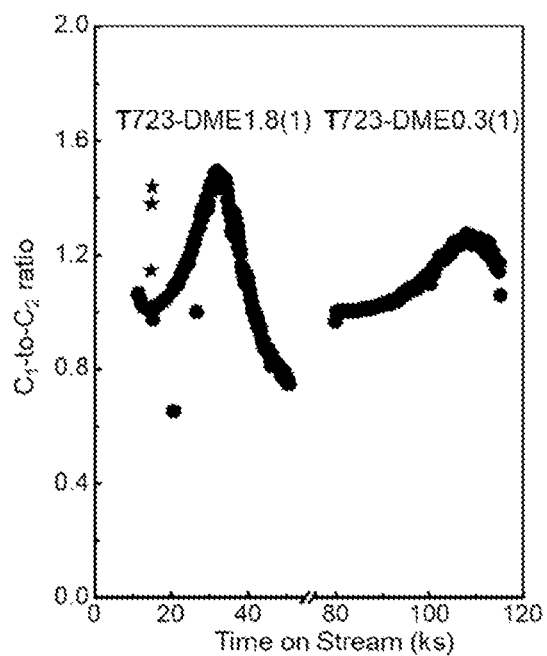


Fig. 6

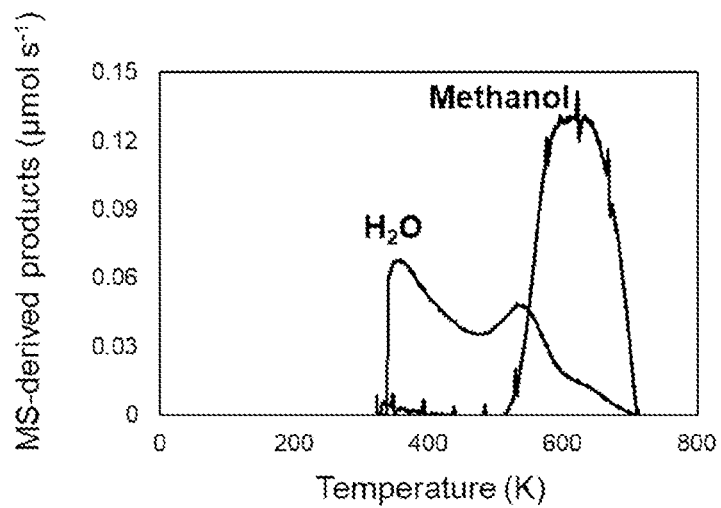


Fig. 7

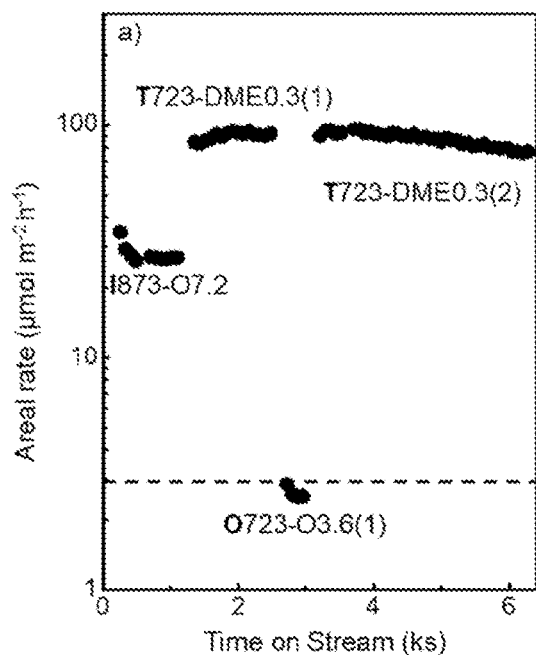


Fig. 8a

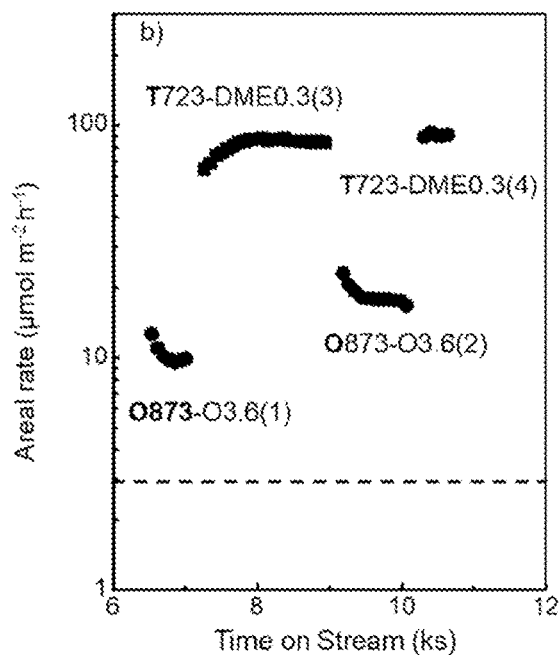


Fig. 8b

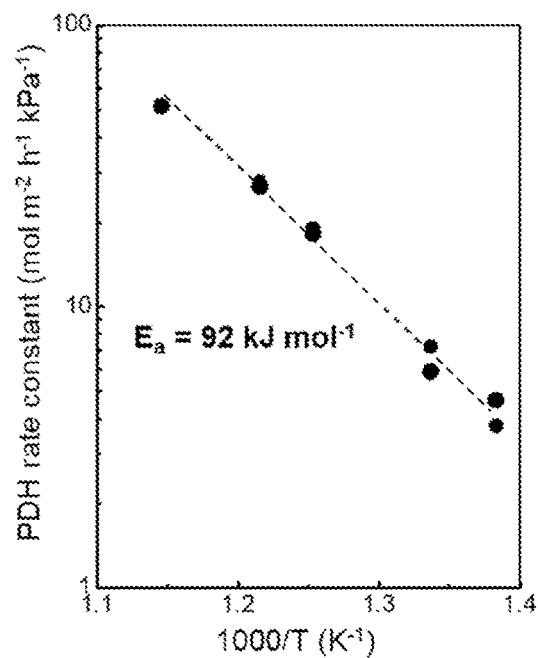


Fig. 9

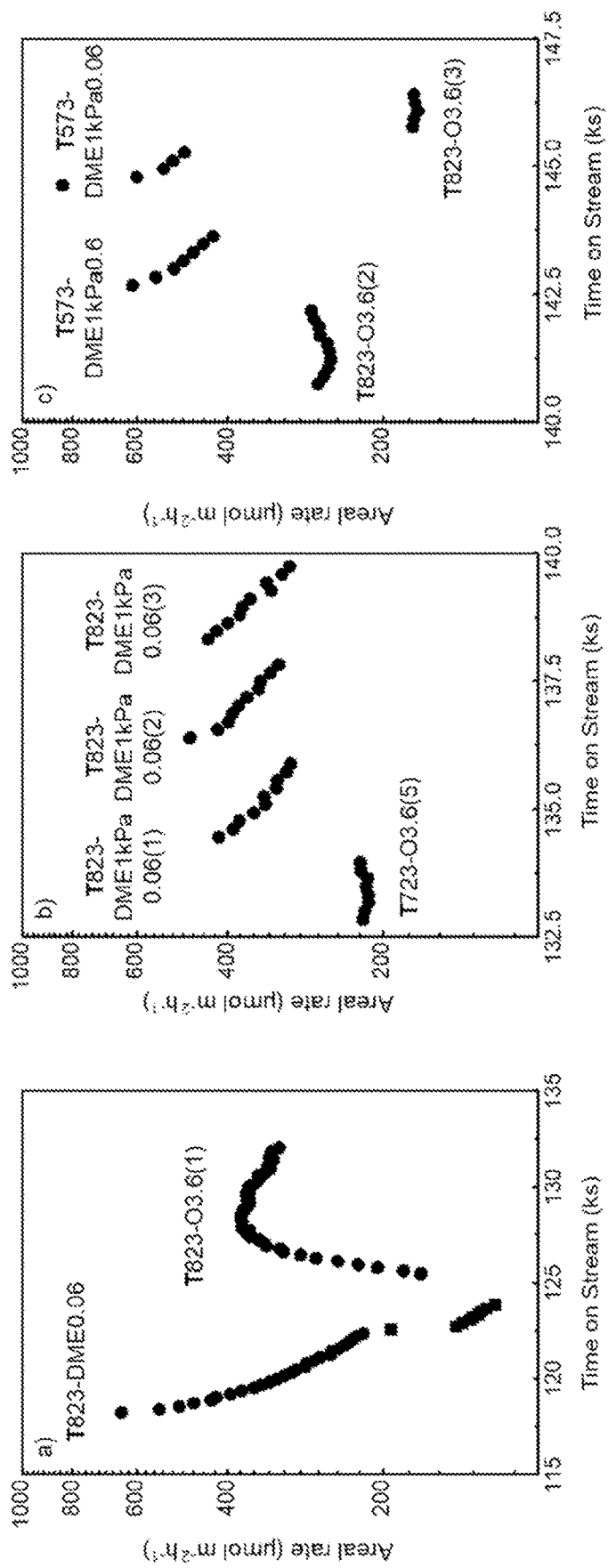


Fig. 10c

Fig. 10b

Fig. 10a

PRETREATING METAL OXIDE CATALYSTS FOR ALKANE DEHYDROGENATION

INTRODUCTION

[0001] Dehydrogenation of light alkanes has been shown to occur on earth-abundant metal oxides. ZrO_2 catalysts have been shown to catalyze propane dehydrogenation (PDH) and exhibit an initial dehydrogenation activity at 823 K of about $5 \text{ mol kg}^{-1}\text{h}^{-1}$, which increases to about $11 \text{ mol kg}^{-1}\text{h}^{-1}$ after 7 h on stream (40 kPa C_3H_8 in N_2) in the absence of co-fed H_2 [1]. CO pretreatment (57 kPa) of ZrO_2 at 823 K for 0.5 h leads to a seven-fold rate enhancement of PDH rates (823 K, 40 kPa C_3H_8 in N_2). CO temperature programmed reduction (CO-TPR, 1 kPa CO) from ambient temperature to 1173 K (1.6 K s^{-1}) shows significant CO consumption between 723 K to 1173 K [1], a temperature regime where the water-gas shift reaction is known to occur [2]; such treatments may remove the strongly adsorbed surface water that exists in its dissociated state [3, 4]. In spite of such observations, previous studies have attributed these effects of thermal treatments (in H_2 or in CO) on reactivity to minority coordinatively unsaturated Zr sites that form during such treatments (in spite of $>500 \text{ kJ mol}^{-1}$ formation enthalpy of O-vacancies on ZrO_2 [1]). Measured activation energy barriers are also much higher ($>130 \text{ kJ mol}^{-1}$) than those derived from theory on ZrO_2 surfaces with O-vacancies ($<30 \text{ kJ mol}^{-1}$) [1].

SUMMARY OF THE INVENTION

[0002] The foregoing observations and inconsistencies in the current literature led us to explore the purposeful treatment of ZrO_2 catalysts with propylene (0.5 kPa) or dimethyl ether (DME, 1-10 kPa); these treatments lead to 2-fold and 40-fold increases in PDH rates (723 K, 13.7 kPa propane and 12.3 kPa H_2) after propylene (0.5 kPa, 723 K, 1.8 ks) and DME treatments (1-10 kPa, 413-823 K, 0.06-3.6 ks), respectively. After DME pretreatment, the maximum rates measured at 723 K, 13.7 kPa propane, and in the presence of H_2 (12.3 kPa) become comparable to those initial rates measured previously at 823 K, 40 kPa propane, and in the absence of H_2 [1]. The pretreatment generates Zr-O site pairs and active sites. The propylene formation derived from stoichiometric reaction between any DME-derived carbon deposits and propane is insignificant, as the carbon deposited during DME treatment, measured via post-reaction oxidation, is about 10-fold less than would be required for its use as a stoichiometric propylene formation reaction. The rate enhancements from alkene/DME may originate from the dehydroxylation/decarboxylation of ZrO_2 catalysts via alkene/DME reactions with $\text{H}_2\text{O}/\text{CO}_2$ occurring at temperatures much lower than those required for treatments in oxidative [1], reductive [1], or inert environments [1], thus allowing the retention of higher reactive surface areas by preventing sintering that is ubiquitous during treatments at such higher temperatures. The method described here provides a novel approach for preparing high surface area oxides devoid of bound H_2O or CO_2 , by avoiding the requirement for severe thermal treatments (i.e., treatments without alkenes/ethers) that dehydroxylate/decarboxylate the oxide surface [6].

[0003] In one embodiment, this invention provides a method of catalytic dehydrogenation of a light alkane gas (e.g. ethane, propane, n-butane, isobutane, pentane) on a

metal oxide (e.g. ZrO_2 , TiO_2 , Al_2O_3) catalyst, the method comprising: (a) pretreating the metal oxide catalyst with dimethylether (DME); and (b) reacting the alkane gas on the catalyst in a dehydrogenation reaction, under conditions wherein the pretreating improves product yields for this dehydrogenation reaction.

[0004] Pretreatment of a catalyst, in the case of the present invention a metal oxide, is to be understood as any process in which a catalyst is contacted with a chemical, combination of chemicals, or a series of chemicals to bring or restore it to a higher activity and/or selectivity state, either before using the catalyst for the intended chemical process or at intervening points in time during use of the catalyst, as shown by the periodic DME treatments that recover the initial activity and involve stopping the PDH reaction and doing again a DME treatment and returning to the PDH feeds. Such pretreatments may be carried out inside or outside the chemical reactor. When used at intervening points during catalyst use, such pretreatments seek to restore all or a portion of the activity and/or selectivity of the catalyst in protocols that may be denoted to those skilled in the art as catalyst regeneration treatments. When used initially upon charging catalysts into a reactor, they may be denoted as activation or selectivation protocols.

[0005] In embodiments:

[0006] the pretreating is performed at a temperature up to 900 K;

[0007] the pretreating is performed at a temperature up to 873 K;

[0008] the pretreating is performed at a temperature up to 823 K;

[0009] the pretreating is performed at a temperature up to 723 K;

[0010] the pretreating is performed at a temperature within a range of 323-900 K;

[0011] the pretreating is performed at a temperature within a range of 323-873 K;

[0012] the pretreating is performed at a temperature within a range of 323-823 K;

[0013] the pretreating is performed at a temperature within a range of 323-723 K;

[0014] the alkane is propane;

[0015] the metal oxide is ZrO_2 ;

[0016] the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step;

[0017] the reaction product is an alkene; and/or

[0018] the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

[0019] The invention encompasses all combinations of the particular embodiments recited herein, as if each combination had been laboriously recited.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1. H_2O desorption molar rate plotted as a function of temperature during temperature programmed oxidation (TPO) of as prepared ZrO_2 catalysts (0.2 g, He and 25 kPa H_2 treated at 873 K) from 323 K to 873 K (0.167 K s^{-1}) and from 873 K to 1173 K.

[0021] FIG. 2. Areal PDH rate ($r_{p,d}$) during propane dehydrogenation reaction on ZrO_2 catalyst (13.7 kPa C_3H_8 , 12.3 kPa H_2 , 723 K, 1723-07.2); color indicates the treatment used before the catalytic reaction (Magenta: O_2 ; dark yellow:

low: propylene;); the dashed line indicates the stable activity measured on ZrO_2 at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 723 K before any followed up treatment(s).

[0022] FIGS. 3a-c. a) Areal rates of PDH ($r_{f,d}$, solid symbols) and C_1 formation (r_{C_1}), and b) C_1 -to- C_2 ratio during propane dehydrogenation reaction on ZrO_2 catalyst (13.7 kPa C_3H_8 , 12.3 kPa H_2 , 723 K, I723-O7.2); color indicates the treatment seen prior to the reaction (magenta: O_2 ; brown: DME); the magenta dash line indicates the stable activity measured on ZrO_2 at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 723 K before any followed up treatment(s) (FIG. 2); c) Arrhenius plot of the non-oxidative PDH rate per mass of literature reported Cr-based (square symbol, 40 kPa C_3H_8), Ru-based (triangle symbol, 40 kPa C_3H_8), Pt-based (diamond symbol, 100 kPa C_3H_8), and ZrO_2 (black circle, 40 kPa C_3H_8 ; the yellow color indicate the ZrO_2 pretreatment in 57 kPa of CO) catalysts, and commercial ZrO_2 without DME treatment measured in this study (black circle, 13.7 kPa C_3H_8), and DME-treated ZrO_2 in this study (brown circle, 13.7 kPa C_3H_8), where open and closed symbols denote 0 and 12.3 kPa H_2 cofed, respectively.

[0023] FIGS. 4a-c. a) Propane dehydrogenation rate per initial surface area of catalyst ($r_{f,d}$, solid symbols) and C_1 formation rate (r_{C_1}), and b) C_1 -to- C_2 ratio during propane dehydrogenation reaction on ZrO_2 catalyst from 20 ks to 55 ks (13.7 kPa C_3H_8 , 12.3 kPa H_2 , 723 K, I723-O7.2); c) time-averaged C_1 -to- C_2 ratio and deactivation rate constant plotted as a function of time period. The Magenta dash line in FIG. 4a indicates the stable activity before measured on ZrO_2 at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 723 K before any followed-up treatment(s).

[0024] FIGS. 5a-c. Areal PDH ($r_{f,d}$, solid symbols) and C_1 formation rate (r_{C_1} , open symbols) measured after a) first DME treatment (i.e., T723-DME1.8); b) second DME treatment (i.e., T723-DME1.8(2)); c) third DME treatment (i.e., T723-DME0.3(1), in brown) and after the oxidative treatment (i.e., T723-O3.6(4), in magenta) during propane dehydrogenation reaction on ZrO_2 catalyst (I723-O7.2) at 723 K; circle symbol (13.7 kPa C_3H_8 , 12.3 kPa H_2), star symbol (13.7 kPa C_3H_8 , 0 kPa H_2), and triangle symbol (0 kPa C_3H_8 , 12.3 kPa H_2); Magenta dash line in FIGS. 5a-5c indicates the stable activity before measured on ZrO_2 at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 723 K before any followed-up treatment(s).

[0025] FIG. 6. C_1 -to- C_2 ratio during propane dehydrogenation reaction on ZrO_2 catalyst measured after first (i.e., T723-DME1.8(1), in brown) and third (i.e., T723-DME0.3(1), in black) DME treatments.

[0026] FIG. 7. H_2O (blue) and methanol (yellow) desorption molar rates plotted as a function of temperature during TPD in 1 kPa dimethyl ether ($0.83 \text{ cm}^3 \text{ s}^{-1}$, 0.5 kPa Ar, balanced with He) of as prepared ZrO_2 catalysts (0.2 g, He treated at 323 K) from 323 K to 723 K (0.03 K s^{-1}).

[0027] FIGS. 8a-b. Areal PDH rates ($r_{f,d}$) of a) after initial O_2 pretreatment at 873 K (I873-O7.2, magenta), 10 kPa DME treatment at 723 K (i.e., T823-DME0.3(x), x=1 or 2, brown), and after O_2 treatment at 723 K (T723-O3.6(1), magenta) and b) after 10 kPa DME treatment at 723 K (i.e., T823-DME0.3(x), x=3 or 4, brown) and after O_2 treatment at 873 K (T873-O3.6(y), y=1 or 2, magenta) measured at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 723 K on ZrO_2 catalyst. Magenta dash line in FIGS. 8 and 8b indicates the stable activity before measured on ZrO_2 at 13.7 kPa C_3H_8 , 12.3

kPa H_2 , and 723 K, right after pretreated in O_2 for 7.2 ks at 723 K (I723-O7.2), as shown in FIG. 2.

[0028] FIG. 9. PDH rate constant (13.7 kPa and 12.3 kPa inlet propane and H_2 pressure), which is the measured PDH areal rate normalized to the averaged propane pressure, obtained on a DME treated as prepared ZrO_2 (1 kPa DME, 0.3 ks) plotted against inverse of temperature.

[0029] FIGS. 10a-c. Areal PDH rate ($r_{f,d}$) measured after a) DME (10 kPa) treatment at 823 K (i.e., T823-DME0.06, brown) and O_2 treatment at 823 K (i.e., T823-O3.6(1), magenta) at 13.7 kPa C_3H_8 , 12.3 kPa (circle) or 0 kPa (square) H_2 and 823 K on ZrO_2 catalyst (I723-O7.2), b) O_2 treatment at 723 K (i.e., T723-O3.6(5), magenta) and DME treatments at 823 K (1 kPa DME, T823-DME1kPa0.06(x), x=1-3, purple) at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 823 K, and c) O_2 treatment at 823 K (i.e., T823-O3.6(y), y=2 or 3, magenta) and DME treatments at 573 K (1 kPa DME, T573-DME1kPa0.06 or T573-DME1kPa0.6, blue) at 13.7 kPa C_3H_8 , 12.3 kPa H_2 , and 823 K.

DESCRIPTION OF PARTICULAR EMBODIMENTS OF THE INVENTION

[0030] Unless contraindicated or noted otherwise, in these descriptions and throughout this specification, the terms “a” and “an” mean one or more, the term “or” means and/or. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein, including citations therein, are hereby incorporated by reference in their entirety for all purposes.

[0031] In these examples, we demonstrate a strategy to remove the irreversible titrants such as H_2O and CO_2 bound on zirconium oxide (ZrO_2) as a result of synthetic protocols used to form the catalyst or during subsequent exposure to ambient air; such removal ultimately increases the activity of ZrO_2 during propane dehydrogenation (PDH) reactions. ZrO_2 catalysts bind H_2O and CO_2 titrants from air; these species cannot be completely removed even at temperature above 1173 K, as shown by our temperature programmed experiments. The high temperature thermal treatments required have also been shown to occlude ZrO_2 catalyst and reduce the accessible surface area, which leads to lower dehydrogenation reactivity on ZrO_2 after such high temperature treatment, despite the removal of these strong surface titrants. Without being bound to any particularly theory, leveraging alkene (e.g. propylene) and ether (e.g., dimethyl ether) reactions with $\text{H}_2\text{O}/\text{CO}_2$ may allow for the removal of surface $\text{H}_2\text{O}/\text{CO}_2$ titrants, thus freeing bare Zr—O sites for alkane dehydrogenation reactions without the destruction of the porous structure and active exposed surface area associated with high temperature treatments, illustrated here using propane dehydrogenation reaction (PDH) as an example, but generally applicable for any reactions catalyzed by stoichiometric Zr—O site pairs. At 723 K, the activity of ZrO_2 catalysts increases by approximately 2-fold and 40-fold after propylene (0.5 kPa) and DME (1-10 kPa) treatment at 723 K for 1.8 ks, respectively. The observed promotional effect on PDH rate does not derive from either the decomposition of carbon deposits or the stoichiometric reaction between carbon deposits and propane, as propylene formation is immediately suppressed when turning off the

propane feed, and the carbon deposited on ZrO_2 via DME treatment is >10 times less than that required for a stoichiometric propylene formation reaction. In particular, DME treatments of ZrO_2 catalysts improve the catalyst's activity at 723 K and 13.7 kPa propane to 5 mol $\text{kg}^{-1}\text{h}^{-1}$ (with 12.3 kPa H_2) and 10 mol $\text{kg}^{-1}\text{h}^{-1}$ (without H_2), which is comparable to values obtained previously at 823 K for ZrO_2 catalysts (7 mol $\text{kg}^{-1}\text{h}^{-1}$, at 40 kPa propane without H_2 [1]). The PDH reactivity measured at 823 K and 13.7 kPa propane after DME treatment becomes 28 mol $\text{kg}^{-1}\text{h}^{-1}$ (with 12.3 kPa H_2), which is more than two-fold higher than on Pt and Cr-based catalysts, even though the latter were measured at higher propane pressure (40 kPa) and in the absence of H_2 inhibitor at 823 K. Temperature-programmed reaction studies using DME (1 kPa) confirmed the successful removal of surface hydroxyls by DME hydration reactions, as methanol, the hydration product of DME, continuously evolves at temperatures above 520 ± 5 K. The PDH activation barrier measured on ZrO_2 catalysts after DME treatment is 92 kJ mol^{-1} , which is much lower than literature reported values (>130 kJ mol^{-1}) [1] but is comparable to the value derived from theoretical calculations (106 kJ mol^{-1}). These findings confirm that PDH reaction proceeds catalytically on a stoichiometric ZrO_2 surface, which is exposed through the assistance of alkene/ether pretreatments. The current strategy leads to reproducible PDH reactivity after DME treatment with or without oxidative treatments. Our methods can be applied to other metal oxide catalysts (e.g., TiO_2 , Al_2O_3) to remove $\text{H}_2\text{O}/\text{CO}_2$ as site titrants, thus exposing their bare surfaces for catalytic reactions without the risks of sintering and loss of active surface area.

[0032] Catalyst Synthesis and Catalytic Rate and Selectivity Measurements:

[0033] The ZrO_2 materials were prepared using a hydrothermal protocol described previously in literature [1] and involves mixing $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ aqueous solutions (12.3 g in 30 ml deionized water) and urea (21.6 g in 30 ml deionized water) followed by subsequent hydrolysis of urea, and increase in pH and the crystallization of ZrO_2 powders (453 K, 20 h), which were dried in ambient air at 383 K overnight. As synthesized catalysts were treated in flowing O_2 and He mixture (2 $\text{cm}^3 \text{g}^{-1}\text{s}^{-1}$, 4% O_2 balanced with He, Praxair) by heating to 723 K (at 0.167 K s^{-1}), holding for 2 h hold, and subsequently purging with flowing He (2 $\text{cm}^3 \text{g}^{-1}\text{s}^{-1}$, UHP, Praxair) in order to remove residual O_2 from the reactor. C_3H_8 (50% C_3H_8 , 10% Ar internal standard, balanced with He, Praxair) and hydrogen (99.999%, Praxair) were introduced into the reactor with He flow (UHP, Praxair) at 723 K. The effluent stream was analyzed by on-line mass spectrometry (MS, MKS) and gas chromatography (GC; Agilent 6890A) using a flame ionization detector (FID) after separation (GS-GASPRO column, Agilent).

[0034] Temperature Programmed Oxidation of ZrO_2 to 1173 K

[0035] The as prepared ZrO_2 was treated at 873 K in He and in H_2/He before temperature programmed oxidation (TPO) in 4 kPa O_2 (balanced with He, 3.35 $\text{cm}^3 \text{g}^{-1}\text{s}^{-1}$). The temperature was increased at 0.167 K s^{-1} from 323 K to 873 K in 4 kPa O_2 and held for 7.2 ks, before a final ramp from 873 K to 1173 K at 0.167 K s^{-1} . After inert and reductive (i.e. 25 kPa H_2 in He) treatments, H_2O continued to evolve from the samples, indicative of H_2O molecules that strongly titrate Zr—O Lewis acid-base pairs, consistent with previous reports [4, 7]. In fact, increasing temperature to 1173 K

is unable to remove all bound water, as water continues to evolve. Previous reports have shown that high-temperature surface annealing removes surface hydroxyls, but it also leads to pore collapse and loss of surface area. Hence, water, which dissociatively adsorbs on ZrO_2 as surface hydroxyls [8], titrates Zr—O site pairs, especially those at the surfaces of monoclinic and tetragonal ZrO_2 which are the most reactive.

[0036] Effect of Propylene Pretreatment on Propane Dehydrogenation Rate at 723 K

[0037] In what follows, we denote the initial pretreatment of ZrO_2 catalyst which has not been exposed to other gases except for air at ambient temperature as “I” and the treatment of ZrO_2 which has been previously exposed to other gases other than air at ambient temperature as “T”. The treatment temperature and duration are denoted as t (t=723-873 K) and δ ($\delta=0-7.2$ ks), respectively. The treatment gaseous condition is denoted as α ($\alpha=\text{O}_2$, py, DME, as abbreviations for O_2 , propylene, and dimethyl ether (DME), respectively); the O_2 , propylene, and DME partial pressure used in these treatments are 4 kPa, 0.5 kPa, and 10 kPa unless otherwise indicated. The number of times that the catalysts have undergone the same treatment is denoted as “(i)” (i=1-5). Thus, It- $\alpha\delta$ and Tt- $\alpha\delta$ (i) denote initial pretreatment at temperature t in α gas for δ and treatment at identical condition but repeated for the i^{th} time. As an example, T723-O3.6(2) indicates the second, O_2 treatment of 3.6 ks at 723 K. Table 1 summarizes the treatment conditions applied in the following discussions.

TABLE 1

Summary of treatment conditions and the associated nomenclature				
Treatment	Duration (ks)	T (K)	Repetition	Nomenclature
O_2 (pre)	7.2	723	—	I723-O7.2
Below for treatments on catalyst I723-O7.2				
propylene	1.8	723	1st	T723-py1.8
O_2	3.6	723	i	T723-O3.6(i)
O_2	3.6	823	i	T823-O3.6(i)
DME	1.8	723	i	T723-DME1.8(i)
DME	0.3	723	i	T723-DME0.3(i)
DME	0.06	823	i	T823-DME0.06(i)
DME1kPa	0.06	823	i	T823-DME1kPa0.06(i)
DME1kPa	0.6	573	i	T573-DME1kPa0.6(i)
DME1kPa	0.06	573	i	T573-DME1kPa0.06(i)
O_2 (pre)	7.2	873	—	I873-O7.2
Below for treatments on catalyst I873-O7.2				
O_2	3.6	723	i	T723-O3.6(i)
O_2	3.6	873	i	T873-O3.6(i)
DME	0.3	723	i	T723-DME0.3(i)

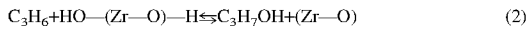
[0038] The forward rate of propane dehydrogenation, $r_{f,d}$, is defined as

$$r_{f,d} = \frac{r_{net,d}}{1 - \eta_d} \quad (1a)$$

$$\text{where } \eta_d = \frac{Q_d}{K_d} \quad (1b)$$

[0039] where $r_{net,d}$, η_d , Q_d , and K_d denote measured net rate, approach to equilibrium, reaction quotient, and equilibrium constant for the PDH reaction at the temperature of interest, respectively. Propane dehydrogenation occurs on

ZrO₂ catalyst (pretreated in 4% O₂/He mixture at 723 K for 2 h, denoted as I723-O7.2) with an initial areal rate of 3.7 μmol m⁻²h⁻¹; this rate decays rapidly and stabilizes at 2.5 μmol m⁻²h⁻¹ after about 1 ks, as shown in FIG. 2. A treatment in propylene (0.5 kPa balanced with He, at 723 K denoted as T723-py1.8), intended to remove surface-bound H₂O/CO₂, led to a 2-fold increase in the initial areal PDH rate (i.e., from 3.7 to 5.5 μmol m⁻²h⁻¹). The purposeful removal of propane (13.7 kPa to 0 kPa) from the inlet stream (between 5.6 ks to 6.7 ks time-on-stream) immediately suppressed propylene formation, indicating that the reactivity enhancement conferred by the propylene treatment reflects the reaction between the actual active sites and propane instead of the stoichiometric decomposition of any potential carbonaceous residues formed during propylene treatment into propylene. We speculate that propylene reacts with H₂O/CO₂ to liberate Zr—O site pairs. As an example, propylene may react with and remove strongly-bound H₂O to form propanols, the hydration product of propylene:



[0040] The rate rapidly decreased to 2.8 μmol m⁻²h⁻¹ within 3 ks, a comparable value to that derived from the original ZrO₂ (I723-O7.2) without propylene treatment. A treatment in O₂ for 3.6 ks (denoted as T723-O3.6(1)) restored the steady-state rates to 2.6 μmol m⁻²h⁻¹, as shown in FIG. 2.

[0041] Effect of Dimethyl Ether (DME) Treatment on Propane Dehydrogenation Rate at 723 K

[0042] After an oxidative treatment, the catalysts were exposed to DME (10 kPa at 723 K for 1.8 ks; T723-DME1.8(1)). This treatment led to an areal PDH rate of 110 μmol m⁻²h⁻¹, a value that is about 40 times higher than those observed after O₂ treatments (i.e., I723-O7.2 and T723-O3.6(1), 2.6 μmol m⁻²h⁻¹). The DME treatment also enhances the formation rate of C₁ (i.e., methane, rate denoted as r_{C1}) and C₂ (i.e., ethylene and ethane, rate denote as r_{C2}). As shown in FIG. 3a, the areal methane formation rate increased by about 280 times to 18 μmol m⁻²h⁻¹ as compared to the sample without the DME treatment (0.06 μmol m⁻²h⁻¹). The C₁/C₂ molar ratio is near unity (FIG. 3b) suggesting that methane forms from propane via hydrogenolysis and cracking, as shown in Equations 3a and 3b, respectively, instead of via the stoichiometric consumption of any DME-derived organic residues.



[0043] The removal of the H₂ co-feed (between 14.5 ks and 15.1 ks) led to an additional two-fold increase of PDH rate (to 246 μmol m⁻²h⁻¹, reflecting the kinetic inhibition of rates by H₂ previously shown for PDH reaction on ZrO₂ at 823-873 K [5]. FIG. 3c shows dehydrogenation rates (normalized by mass) on ZrO₂ catalyst after DME treatment and also on previously reported Cr [9], Pt [10-12], Ru [9], and ZrO₂ [1] based catalysts. The initial PDH rates (10 mol kg⁻¹h⁻¹) after T723-DME1.8(1) treatment (13.7 kPa C₃H₈ without added H₂ at 723 K) is similar to those reported at much higher temperatures on other catalysts at 823-828 K and even higher C₃H₈ pressures (40-100 kPa, Pt: 14.5 mol kg⁻¹h⁻¹; Cr: 13 mol kg⁻¹h⁻¹; Ru: 10.7 mol kg⁻¹h⁻¹; ZrO₂: 7.1 mol kg⁻¹h⁻¹).

[0044] The rate increase upon removal of H₂ also leads to a two-fold decrease in C₁ formation rates (FIG. 3a), while

the C₁/C₂ ratio increased from about unity to about 1.5 (FIG. 3b). The reasons for these trends remain unclear, since H₂ has been reported to preferentially remove reaction-derived organic residues as CH₄ from zeolitic solid acids that show alternate dehydrogenation routes on such residues [13].

[0045] The reintroduction of H₂ (12.3 kPa) restored dehydrogenation and C₁ (and C₂) formation rates to those measured before H₂ removal from the inlet stream (FIG. 3a). The C₁/C₂ molar ratios return to values near unity and increase slightly with time-on-stream (from 0.97 to 1.07) concurrently with a slight decrease in dehydrogenation and C₁ formation rates in a manner consistent with first-order deactivation process:

$$\frac{r_i(t_2)}{r_i(t_1)} = \exp(-k_{i,deac}^{1st} \cdot (t_2 - t_1)) \quad (4)$$

[0046] Here, r_i, k_{i,deac}^{1st}, and t_m denote rates (i=f,d and C1 for dehydrogenation rate and C₁ rates, respectively), deactivation rate constant of reaction i, and time-on-stream at any time m, respectively. The values of k_{f,d,deac}^{1st} and k_{C1,deac}^{1st} values are 4.1×10⁻²ks⁻¹ and 3.5×10⁻¹ks⁻¹, respectively. C₁ formation rates decrease more prominently with time-on-stream than dehydrogenation rates, leading to a concomitant increase in dehydrogenation selectivity (i.e., instantaneous selectivity ratio, r_{f,d} (r_{C1})⁻¹, from 6 to 72 in the 11-19 ks period).

[0047] After 20 ks on stream (20-40 ks), PDH and methane formation rates continue to decrease as a function of time-on-stream, albeit more sharply for methane formation (FIG. 4a). The PDH rate eventually asymptotically approaches a value that is comparable to those measured without DME/propylene treatments. Excess amount of methane formation occurs, when considering stoichiometric cracking and hydrogenolysis reactions (in Eqs. 3a and 3b, respectively), leading to the C₁/C₂ molar ratios larger than unity at 20-40 ks times on stream. The excess methane suggests the removal of carbonaceous deposits in the form of methane catalyzed by Zr—O site pairs, previously seen during propane dehydrogenation on zeolites at comparable conditions [13]. These carbonaceous deposits are likely derived from the coupling of alkenes and deeper dehydrogenation products, which represent the amount of alkene products that do not escape the catalyst's surface but accumulates in a semi-batch form. After 40 ks on stream, the rate of deactivation decreases and C₁/C₂ molar ratios become smaller than unity (FIG. 4b) with reasons not clearly understood.

[0048] We define time period of time-on-stream as: 0) 11-19 ks, 1) 20-25 ks, 2) 25-30 ks, 3) 30-35 ks, 4) 35-40 ks, 5) 40-45, and 6) 45-51 ks. FIG. 4c plots the averaged k_{f,d,deac}^{1st} and C₁-to-C₂ molar ratios within each time period as a function of the corresponding time period. It can be seen from FIG. 4c that the deactivation rate constant almost commensurately (except for time period 4)) increases and decreases with the value of the C₁-to-C₂ molar ratio. These observations lead us to speculate that the carbonaceous deposits titrate Zr—O site pairs and are the cause of on-stream deactivation. As the amount of carbonaceous deposits increase initially, the observed deactivation rate constants and C₁-to-C₂ molar ratios in time periods 0)-to-3) also increase. Then, as the carbonaceous deposit titrates Zr—O site pairs that catalyze the PDH, propane cracking/hydroge-

nation, and the hydrogenolysis of the carbonaceous deposit, the PDH rate, $k_{f,d,deac}^{1st}$ and C_1 -to- C_2 molar ratios decreases, approaching to a steady-state value in the time period of 4)-to-6). The PDH rate eventually drops down to the activity measured after initial oxidative treatment, suggesting that the carbonaceous deposit does not titrate all the ZrO_2 sites.

[0049] In summary, these results suggest that alkene/DME treatments likely lead to rate enhancements via the reactions between alkene/DME and H_2O/CO_2 . The decrease in rate after DME treatments may reflect the gradual accumulation of carbonaceous deposit.

[0050] Sequential Dimethyl Ether (DME) Treatment Effects on Propane Dehydrogenation Rate at 723 K

[0051] The reproducibility of DME treatments were examined by subsequent treatments (DME, 10 kPa for 1.8 ks, T723-DME1.8(2)), after 4% O_2/He for 3.6 ks (T723-O3.6(2)). FIGS. 5b and FIG. 5c show the PDH areal rate and C_1 formation rate measured after T723-DME1.8(2) and T723-DME0.3(1), respectively; those measured after the first of such treatment is shown in FIG. 5a (shown also in FIG. 4a). The T723-O3.6(2) and T723-DME1.8(2) protocols led to similar initial rates ($130 \mu\text{mol m}^{-2}\text{h}^{-1}$ and $27 \mu\text{mol m}^{-2}\text{h}^{-1}$ vs. $110 \mu\text{mol m}^{-2}\text{h}^{-1}$ and $18 \mu\text{mol m}^{-2}\text{h}^{-1}$ for dehydrogenation and C_1 rates after the first and second treatments, respectively). The removal of propane from the inlet stream (57.2-59.6 ks) immediately suppressed all propylene formation but not all the C_1 formation, consistent with the presence and gradual removal of reaction-derived organic residues as C_1 . Restoring the propane flow (from 0 kPa to 13.7 kPa) recovered the propane dehydrogenation rate (continuing previous rate trend, increased from 0 to $75 \mu\text{mol m}^{-2}\text{h}^{-1}$) and the methane formation rate (continuing previous rate trend, increased from 0 to $1.2 \mu\text{mol m}^{-2}\text{h}^{-1}$).

[0052] Repeating the O_2 treatment for 3.6 ks (T723-O3.6(3)) and following this with a DME treatment (10 kPa) for a shorter duration of 0.3 ks (T723-DME0.3(1)) leads to initial PDH and methane areal rates of $189 \mu\text{mol m}^{-2}\text{h}^{-1}$ and $38 \mu\text{mol m}^{-2}\text{h}^{-1}$, respectively, as shown in FIG. 5c, which are even higher than those obtained after previous DME treatments of longer duration (i.e., T723-DME1.8(1) and T723-DME1.8(2)). Such trends and observations may reflect a hydrodynamic delay upon introduction of reactants, leading to initial rate measurements that do not reflect the intended steady-state propane and H_2 pressures. The deactivation of the catalyst, as reflected by the decrease in PDH areal rate, is less significant after DME treatment for 0.3 ks compared with those after DME treatment for 1.8 ks. FIG. 6 plots the C_1 -to- C_2 ratio as a function of time-on-stream for those measured after T723-DME1.8(1) and T723-DME0.3(1). Although C_1/C_2 molar ratios start at unity in both cases, they much more gradually and to a lesser extent after the T723-DME0.3(1) than after the T723-DME1.8(1) treatment, suggesting that the carbonaceous deposit accumulation in T723-DME0.3(1) treatment is less significant, thereby leading to the catalyst's longer life time. The DME partial pressure and treatment duration effects on the PDH rate and catalyst lifetime will be part of our future study.

[0053] After T723-DME0.3(1) and PDH rate measurements, the ZrO_2 catalyst was regenerated again via oxidative treatment (T723-O3.6(4)). The propane dehydrogenation rate shows slightly lower areal rates of $2.2 \mu\text{mol m}^{-2}\text{h}^{-1}$ compared with those stable rates measured after the initial oxidative treatment (T723-O7.2, $2.6 \mu\text{mol m}^{-2}\text{h}^{-1}$).

[0054] The CO_2 evolved during the oxidative treatments (i.e., T723-O3.6(2), T723-O3.6(3), and T723-O3.6(4)) provides quantitative information regarding the cumulative amount of reaction-derived organic residues formed and left on the catalyst from (i) DME treatment and (ii) propane dehydrogenation reactions. Table 2 shows the amounts of CO_2 evolved during each O_2 treatment. DME treatments (0.3-1.8 ks) together with propane dehydrogenation reaction deposit 2.5×10^{-4} mol (18 C nm^{-2}) to 2.8×10^{-4} mol (21 C nm^{-2}) of carbon on the ZrO_2 catalyst, whereas a direct DME treatment for 0.3 ks (i.e., T723-DME0.3(2)), without performing propane dehydrogenation reaction, leads to the formation of 1.2×10^{-4} mol of carbon (9 C nm^{-2}).

TABLE 2

Summary of CO_2 generated during treatment in 4 kPa O_2 (balanced in He) after various DME treatments before or after propane dehydrogenation reactions			
Entry	Treatment	Carbon source	CO_2 per surface area (molecule nm^{-2})
1	T723-O3.6(2)	T723-DME1.8(1); PDH reaction	18
2	T723-O3.6(3)	T723-DME1.8(2); PDH reaction	21
3	T723-O3.6(4)	T723-DME0.3(1); PDH reaction	20
4	T723-O3.6(5)	T723-DME0.3(2)	9

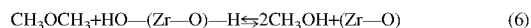
[0055] Equation 5 defines the excess molar of propylene, X, formed from the catalyst after the DME treatment:

$$X = \int_{t_0}^{t_1} (r_{f,d,DME}(t) - r_{f,d,O}) dt \cdot \varepsilon \quad (5)$$

[0056] where $r_{f,d,DME}(t)$, $r_{f,d,O}$, and ε are the forward dehydrogenation rate after DME treatment at any time on stream t, the steady-state forward dehydrogenation rate after O_2 pretreatment (i.e., T723-O7.2), and the catalyst surface area, respectively. For T723-DME1.8(1), X is 3.5×10^{-3} mol (i.e., 263 nm^{-2}), which is more than one order of magnitude higher than the carbon deposited by DME treatment (Entry 4, Table 2). If the reaction between carbonaceous deposit and propane occurs via a stoichiometric reaction, the H-atom derived from propane dehydrogenation is sufficient to hydrogenate all the deposited carbon from DME treatment (i.e., 9 nm^{-2}) into CH_4 with 6.0×10^{-3} mol of excess. Therefore, we conclude that propane dehydrogenation occurs catalytically on the ZrO_2 surfaces.

[0057] Effect of Dimethyl Ether (DME) Treatment on Water Removal Revealed by Temperature Programmed Desorption (TPD)

[0058] The as prepared ZrO_2 was treated at 323 K in He for 7.2 ks before TPD. The temperature was increased at 0.03 K s^{-1} from 323 K to 723 K in 1 kPa DME (balanced with He, $0.83 \text{ cm}^3\text{s}^{-1}$). The H_2O and methanol evolution profile, plotted against the temperature, is shown in FIG. 7. As temperature increases, water desorption occurs at 373 K and 523 K, whereas methanol formation begins to occur at 520 K. The formation of water suggests the stoichiometric reaction of DME and surface hydroxyls occurs via:



[0059] The methanol evolution clearly demonstrates the successful removal of water by the DME hydration reaction. This removal of water exposes stoichiometric Zr—O site pairs, as suggested in Equation 6. In contrast to what has been shown in FIG. 1, both methanol and water signals decrease to below detection limits at 723 K, reflecting the complete removal of water (and surface hydroxyls) via DME hydration at 723 K.

[0060] Origin of Rate Enhancement from DME Treatment and Apparent Barrier Measurements of PDH Rate on DME-Cleaned ZrO₂ Surfaces

[0061] Thermal treatment (i.e., treatments in the absence of alkene/ethers) of a new load of ZrO₂ catalyst at 873 K for 7.2 ks (I873-O7.2) causes the initial propane dehydrogenation to increase by about ten-fold to 26 $\mu\text{mol m}^{-2}\text{h}^{-1}$, as shown in FIG. 8, compared to the catalyst pretreated in O₂ at 723 K for the same duration (I723-O7.2, FIG. 1, 2.6 $\mu\text{mol m}^{-2}\text{h}^{-1}$). A subsequent DME treatment at 723 K for 0.3 ks (T723-DME0.3(1)) increases the rate to 94 $\mu\text{mol m}^{-2}\text{h}^{-1}$, which is slightly smaller than that measured in previous load after T723-DME1.8(1) (110 $\mu\text{mol m}^{-2}\text{h}^{-1}$, FIG. 2a) for the sample pretreated at 723 K (I723-O7.2). We speculate that the high temperature thermal treatment is able to generate more active Zr—O site pairs via water/CO₂ removal, as clearly indicated in FIG. 1, but such high temperature treatment simultaneously collapses the porous structure of the ZrO₂ and leads to decreased surface areas as previously reported for ZrO₂ [6]. As a result, the PDH areal rate after DME treatment at 723 K are smaller for the new load catalysts (FIG. 8, initial oxidative treatment at 873 K) than those measured for the previous load of catalysts (FIG. 2, initial oxidative treatment at 723 K).

[0062] For the new load of catalyst (i.e., I873-O7.2), a follow-up O₂ treatment at 723 K (T723-O3.6(1)) causes the PDH rate (13.7 kPa propane, 12.3 kPa H₂, 723 K) to decrease to 2.5 $\mu\text{mol m}^{-2}\text{h}^{-1}$, which is comparable to the rate measured after an initial O₂ pretreatment at 723 K of the previous load (i.e., 2.6 $\mu\text{mol m}^{-2}\text{h}^{-1}$, I723-O7.2, FIG. 1). As the oxidative treatments remove carbon deposits derived from previous DME treatment and/or PDH rate measurements as H₂O and CO₂, results in FIG. 8b suggest that (i) the H₂O and/or CO₂ generated during oxidative treatment (T723-O3.6) titrates the Zr—O sites and (ii) an oxidative treatment at 873 K liberates more vacant Zr—O site pair than that at 723 K. A subsequent DME treatment for 0.3 ks (T723-DME0.3(2)), however, restores the propane dehydrogenation activity to the identical level as previous DME treatment (T723-DME0.3(1)), in no regards of the PDH activity from previous measurement after oxidative treatment. This observation further confirms that DME can regenerate Zr—O site pairs in a reproducible manner.

[0063] Attempting to recover the Zr—O site pairs via oxidative treatments at 873 K with a He purge at 873 K for 3.6 ks (T873-O3.6(1)) or overnight (T873-O3.6(2))) lead to areal PDH rates of 10 $\mu\text{mol m}^{-2}\text{h}^{-1}$ and 17 $\mu\text{mol m}^{-2}\text{h}^{-1}$, respectively. These oxidative treatments at 873 K did not fully recover of the PDH rate after initial oxidative treatment (i.e., 26 $\mu\text{mol m}^{-2}\text{h}^{-1}$, after I873-O7.2). We speculate that the extent of regeneration of Zr—O site pairs via oxidative and a following He treatments at 873 K depends on (i) the amount of carbonaceous residue formed from previous treatment(s) and PDH rate measurements, which dictates the amount of CO₂ and H₂O formed during the oxidative treatment, and (ii) the duration at which the catalyst resides in

He. The inconsistent rate measured after oxidative treatments reflects the inconsistent amount of Zr—O site regenerated after these treatments. The DME treatments at 723 K (T723-DME0.3(i), i=1-4), however, always lead to reproducible reactivities of about 90 $\mu\text{mol m}^{-2}\text{h}^{-1}$, irrespective of the PDH rate measured after preceding oxidative treatments. These observations further confirm that DME can remove irreversible titrants of H₂O and CO₂ generated during oxidative treatments and exposes ZrO₂ surface to an identical extent.

[0064] We further corroborate the effect of DME treatments by measuring the apparent PDH barrier on a DME treated ZrO₂ catalyst. The PDH rate was measured at 13.7 kPa propane pressure and 12.3 kPa H₂ pressure from 723 K to 873 K. The PDH rate constant, obtained by normalizing the measured PDH rate by the arithmetic average of the inlet and outlet propane pressure, is plotted in an Arrhenius plot (FIG. 9). This measured value is more than 40 kJ mol⁻¹ smaller than what has been reported on ZrO₂ catalysts [1] but appears comparable to the value derived from density functional theory (DFT-D3) calculation derived barrier (106 kJ mol⁻¹) of PDH on a stoichiometric monoclinic ZrO₂ (-111) surface. We suspect that previous measurements in the absence of DME treatments are unable to expose Zr—O site pairs at lower temperatures (e.g., <823 K). Thus, these previous reports underestimate the PDH turnover rates to a greater extent at lower temperatures and hence overestimate the apparent PDH barrier. The consistency between experimentally and theoretically derived barrier corroborates that DME (and alkene) hydration reaction removes water bound to Zr—O site pairs and exposes these site pairs as the active sites for PDH reaction.

[0065] Effect of Dimethyl Ether (DME) Treatment on Propane Dehydrogenation Rate at 823 K and the Operation in Cyclic Mode

[0066] Treatment of DME (10 kPa) at 823 K for a duration of 0.06 ks (T823-DME0.06) leads to an initial PDH rate measured at 13.7 kPa propane, 12.3 kPa H₂, and 823 K of 643 $\mu\text{mol m}^{-2}\text{h}^{-1}$, as shown in FIG. 10a. The catalyst then rapidly deactivates with the first-order deactivation rate constant of $2.2 \times 10^{-1} \text{ ks}^{-1}$. Increasing the H₂ partial pressure from 12.3 kPa to 50 kPa leads to an instantaneous decrease in the rate from 218 $\mu\text{mol m}^{-2}\text{h}^{-1}$ to 144 $\mu\text{mol m}^{-2}\text{h}^{-1}$ (FIG. 10a), which is consistent with the H₂ inhibition observed at 723 K (FIG. 3a). Areal propane dehydrogenation rates increase to 168 $\mu\text{mol m}^{-2}\text{h}^{-1}$ following an oxidative treatment at 823 K for 3.6 ks (T823-O3.6(1)). The PDH rate then increases gradually to a maximum at 375 $\mu\text{mol m}^{-2}\text{h}^{-1}$ before decaying to 318 $\mu\text{mol m}^{-2}\text{h}^{-1}$ with time-on-stream. Oxidative treatment at 723 K for 3.6 ks (T723-O3.6(5)) causes the PDH rate at about 220 $\mu\text{mol m}^{-2}\text{h}^{-1}$ at 823 K, as shown in FIG. 10b. The PDH rate is comparable with that obtained initially after T823-O3.6(1) (168 $\mu\text{mol m}^{-2}\text{h}^{-1}$, FIG. 10a), but it does not undergo similar transient after T823-O3.6(1). These inconsistent areal PDH rate, obtained after oxidative treatments, suggests that the number of exposed Zr—O site pairs may vary according to previous treatment conditions or the duration of PDH rate measurements.

[0067] The following three direct DME treatments in FIG. 10b with lower DME pressure (1 kPa, denoted as T823DME1kPa(x), where x=1, 2, or 3) enhances the PDH rate to about 420 $\mu\text{mol m}^{-2}\text{h}^{-1}$ each time. After each DME treatment, the PDH rate rapidly decreases to about 300 μmol

$\text{m}^{-2}\text{h}^{-1}$ within 1.5 ks, as shown in FIG. 10b; the first-order deactivation rate constant is about $2.2\text{--}2.5 \times 10^{-1} \text{ ks}^{-1}$. These observations lead us to conclude that (i) part of the reason for the on-stream deactivation is mediated by the water poisoning from ppm levels of water in the reactant stream, and (ii) the DME treatments are highly reproducible and can regenerate Zr—O site pairs even without oxidative treatments. The PDH rate does not, however, recover to that measured after the first DME treatment at 823 K (i.e., $643 \mu\text{mol m}^{-2}\text{h}^{-1}$, T823-DME0.06).

[0068] Subsequent oxidative treatments (T823-O3.6(2)) leads to an areal PDH rate of $267 \mu\text{mol m}^{-2}\text{h}^{-1}$. The followed up DME treatments at 573 K for 0.6 ks (T573-DME1kPa0.6) or 0.06 ks (T573-DME1kPa0.06) lead to the areal PDH rates of $611 \mu\text{mol m}^{-2}\text{h}^{-1}$ and $837 \mu\text{mol m}^{-2}\text{h}^{-1}$, respectively, which are comparable (or even higher) to that obtained after T823-DME0.06. These results suggest that DME treatments at 573 K, 1 kPa of DME with durations of 0.06 ks are effective and lead to the removal of H_2O and CO_2 . The final, oxidative treatment at 823 K for 3.6 ks (T823-O3.6(3)) leads to a PDH rate of about $175 \mu\text{mol m}^{-2}\text{h}^{-1}$. Once again, the oxidative treatments (e.g., T823-O3.6(1), T823-O3.6(2), and T823-O3.6(3)) do not reset the ZrO_2 catalyst to a consistent starting point but instead exhibit a memory effect.

[0069] In conclusion, the DME treatment promotes PDH rate but less significantly at 823 K; the repetitive DME treatments reset the PDH rate in a consistent manner; the DME treatment is able to remove water and regenerate active sites at temperature as low as 573 K with lower DME exposure (i.e., 1 kPa).

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1. A method of catalytic dehydrogenation of a light alkane gas on a metal oxide catalyst, the method comprising steps:

(a) pretreating the metal oxide catalyst with dimethylether (DME); and

(b) reacting the alkane gas catalytically on the catalyst in a dehydrogenation reaction, under conditions wherein the pretreating improves product yield of the reaction.

2. The method of claim 1 wherein the pretreating is performed at a temperature within a range of 323-873 K.

3. The method of claim 1 wherein the pretreating is performed at a temperature of 723 K.

4. The method of claim 1, wherein the metal oxide is ZrO_2 .

5. The method of claim 1, wherein the alkane is propane.

6. The method of claim 1, wherein the reaction product is an alkene.

7. The method of claim 1, wherein:

the alkane is propane; and

the reaction product is an alkene.

8. The method of claim 1, wherein:

the metal oxide is ZrO_2 .

the alkane is propane; and

the reaction product is an alkene.

9. The method of claim 1, wherein:

the pretreating is performed at a temperature within a range of 323-873 K;

the metal oxide is ZrO_2 .

the alkane is propane; and

the reaction product is an alkene.

10. The method of claim 1, wherein:

the pretreating is performed at a temperature of 723 K;

the metal oxide is ZrO_2 .

the alkane is propane; and

the reaction product is an alkene.

11. The method of claim 1, wherein the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step.

12. The method of claim 7, wherein the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step.

13. The method of claim 8, wherein the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step.

14. The method of claim 9, wherein the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step.

15. The method of claim 10, wherein the pretreating improves product yield at least 2-fold compared with a comparable reaction without the pretreating step.

16. The method of claim 1, wherein the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

17. The method of claim 7, wherein the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

18. The method of claim 8, wherein the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

19. The method of claim 9, wherein the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

20. The method of claim 10, wherein the pretreating step further comprises a pretreatment with oxygen prior to or following the pretreatment with DME.

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