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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b00986 • Publication Date (Web): 10 Jul 2017 Downloaded from http://pubs.acs.org on July 16, 2017

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Hydrodeoxygenation of Furylmethane Oxygenates to Jet and Diesel Ranged Fuels: Probing the Reaction Network with Supported Palladium Catalyst and Hafnium Triflate Promoter

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Abstract

Catalytic hydrodeoxygenation of furylmethane oxygenates to high carbon branched chain jet and diesel fuel ranged alkanes at mild reaction conditions is a promising strategy for energy-efficient production of fuels with minimal C-C cracking to undesired products. Here, we report that a strong Lewis acidic promoter can overcome the energy barrier for furylmethanes hydrodeoxygenation at lower temperature. Furan rings of furylmethanes are first hydrogenated to fully saturated cyclic ethers by a hydrogenation catalyst, which then undergo facile ring-opening and deoxygenation by the promoter. A cyclic intermediate between etheric 'O' and the Lewis acidic metal center, assisted by the triflate ligand of the promoter, is formed in the ring-opening step. Probing the reaction pathway with symmetric single furan ring surrogate molecules suggest that the promoter is necessary for the ring-opening. Deoxygenation of ring-opened oxygenates takes place faster for single ring furan surrogates than the multi-furan rings furylmethanes. Maximum 97% jet fuel ranged alkanes with 93% selectivity in $C_{15}H_{32}$ and $C_{14}H_{30}$ is achieved from C_{15} -furylmethane at optimal conditions. The yield and selectivity of alkanes with desired carbon numbers can be tuned by two-stage heating, and using furylmethanes with tailored carbon-chain, furan numbers and the carbon center that minimizes C-C cracking.

Keywords: hydrodeoxygenation, furylmethane, jet fuel, branched alkane, 2-5-dimethylfuran, ring-opening.

Introduction

According to International Energy Agency's Oil Market Report, global crude oil consumption in 2015 reached about 1.4 trillion gallons of which the United States alone consumed about one fifth. Direct carbon emissions from crude oil (~92 g CO₂ E/MJ) are high when compared with renewable fuel alternative, e.g., bioethanol from the 1st generation biomass.¹ The United States Renewable Fuel Standard (RFS) act mandates blends of renewable biofuels with conventional fuel to minimize carbon emissions, leading to a rapid expansion of bioethanol and other high octane advanced biofuels production from non-food lignocellulosic biomass. Among advanced biofuels, production of high carbon branched and long chain alkanes for jet (C_{8-15}) or diesel (C_{12-22}) ranged fuels has received considerable attention in recent years because the US Federal Aviation Administration (FAA) has set a goal for the US aviation industry to consume renewable jet fuel from 2018.² As a result, extensive research and commercialization activities have been initiated to meet increased renewable jet fuels demand.³ Currently, renewable jet fuels are produced via alcohol to jet (ATJ), hydroprocessing esters and fatty acids (HEFA), Fischer Tropsch (FT), hydrotreated depolymerized cellulosic jet (HDCJ) and catalytic conversion of sugars-to jet (CCSTJ) processes.⁴ Among these processes, the CCSTJ pathway is of great interest because of abundant supply of non-food biomass, low temperature processing compared to other high temperature hydrotreatment and high product selectivity.

A major limitation in the direct conversion of carbohydrates to fuels is the low carbon sugar units (C5/C6) in cellulose and hemicellulose, which are unsuited for jet or diesel ranged fuels. As a result, direct catalytic hydroprocessing of lignocellulose or cellulose involving depolymerization, dehydration and hydrodeoxygenation (HDO) pathways produce low carbon alkanes (hexane and pentane) as the major products.⁵ A strategy for building such fuel precursors is C-C coupling of low carbon biomass intermediates by hydroxyalkylation/alkylation (HAA),⁶ Garcia-Gonzalez (GG)⁷ and aldol condensation reactions.⁸ Subsequent hydrogenation, ringopening (RO), and deoxygenation of the resulting molecules over heterogeneous catalysts can produce alkanes of desired carbon numbers.

Catalytic HDO of such fuel precursors over metal catalysts, e.g., $Pt/C/TaOPO_4$,⁹ Pd/Zeolite- β ,¹⁰ Pt/C-Pt/TiO₂,¹¹ Pd/H-ZSM-5, Pd/SiO₂-Al₂O₃, Pd/Al₂O₃,¹² Pt/MCM-41,¹³ Ni-Mo₂C/SiO₂^{14a} and Pt/C,^{6a} has been reported. These reactions involve multiple steps (hydrogenation, RO, deoxygenation) and severe reaction conditions (up to 400 °C). For example,

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Pt/C alone could not fully deoxygenate the precursor without TaOPO₄ at 300 °C.⁹ While deoxygenation of the precursor occurred over Pt/C in a flow reactor at higher temperature (350 - 400 °C) and H₂ pressure of 50 bar,^{6a, 11} Pt on an acidic supports (Al₂O₃, TiO₂) enhanced C-C cracking at these severe conditions.^{6a} C-C cracking was also observed with the metal-acid bifunctional catalysts containing weakly acidic sites, especially at temperatures above 300 °C and H₂ pressure of 40-50 bar.^{6a} Gradient heating of the reaction mixture from 120 °C to 350 °C in the flow reactor suppressed C-C cracking slightly (5-7%). However, mechanistic understanding, such as the order in which hydrogenation, RO and deoxygenation steps take place, remains unclear. Recently, Pd/NbOPO₄ has been reported as an efficient catalyst for C₁₅ branched alkanes.^{14b}

To overcome the challenges associated with high temperature HDO and to minimize the energy input of the process, an alternate strategy has been devised to deoxygenate the precursors at reasonably lower temperature (<225 °C) using a physical mixture of a hydrogenation catalyst (Pd/C) and a promoter, e.g., a metal triflate salt.¹⁵ The authors proposed the reaction progressed via RO of unsaturated furan ring to a ketonic intermediate followed by HDO of C=O bonds, and that ring hydrogenation of the furan first results in a dead-end intermediate. In contrary, Song et al.¹⁶ observed that ring hydrogenation of furan occurs first and the triflate salt acts as an oxygen remover in opening the hydrogenated ring.

Recently we developed a novel and efficient catalytic pathway to synthesize oxygenated furylmethane type fuel precursors (Scheme 1) of carbon numbers 12-21 with 95% yield via HAA reaction of low carbon biomass furans and carbonyl compounds.¹⁷ This reaction, operating at low temperature (60 °C) and neat conditions without involving any complex separation and purification steps, is scalable to produce fuel precursors. Here, we use a C_{15} fuel precursor, 5,5′-bis(2-methylfuranyl)furan-2-ylmethane (**1**) as a model furylmethane to study HDO with the Pd/C catalyst in the presence of a small amount of Hf-triflate (Hf(OTf)₄) salt, to elucidate sequence of steps (hydrogenation, RO and deoxygenation). Compound **1** is an ideal model substrate because it produces C_{15} branched alkane, which is preferred for jet fuel application due to their better cold flow properties than their straight chain analogues (*n*-alkanes).

We show that **1** undergoes hydrogenation of furan rings to fully saturated furan derivative with branched carbon backbone that is transformed to a hydroxylated intermediate via RO and eventually to C_{15} and C_{14} alkanes upon deoxygenation. We demonstrate that RO of furan ring

and cleavage of C–O bonds are the key steps in post-hydrogenation of furan rings. Single ring furan molecules, 2,5-demethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF) were used as probe systems to assess the reaction network. The role of $Hf(OTf)_4$ in RO of furan moieties is elucidated by comparing its activity with the other Hf-salts, zeolite and blank (without Hf-salt) systems. The reaction conditions are systematically optimized to achieve maximum 97% yield of branched alkanes containing over 90% C₁₅ and C₁₄ alkanes as the major products. Structurally diverse fuel precursors (2-4) are used to understand how the nature of carbon backbone of furylmethane influences RO, HDO and alkanes selectivity.



Scheme 1. Hydrodeoxygenation (HDO) of furylmethanes to branched chain alkanes using Pd/C-Hf(OTf)₄ as catalyst.

Experimental Section

Chemicals. Furylmethanes **1**, **2**, **3**, and **4**, were synthesized by catalytic HAA of 2-methylfuran (2-MF) with furfural, butanal, acetone, and 5-hydroxymethylfurfural (HMF), respectively, using improve graphene oxide (IGO) as a catalyst under neat condition by following our earlier publication.¹⁷ In brief, 2-MF and a carbonyl compound were reacted in 2:1 molar ratio in the presence of the IGO catalyst at 60 °C for 6 h without any solvent. After reaction, the catalyst was separated by centrifugation and the condensation products were collected by decantation. Pd₁₀/C (10 wt% Pd), hafnium triflate (Hf(OTf)₄), cyclohexane, hafnium chloride (HfCl₄), hafnium oxide (HfO₂), triflic acid (TfOH), 2,5-dimethylfuran (DMF), 2,5-dimethyltetrahydrofruan (DMTHF) were purchased from Sigma-Aldrich, USA. H-BEA-25 was purchased from Zyolist, USA. Standard C₈ – C₁₉ alkane samples (1000 μ L/g) and standard oil samples (C₁₈ - C₃₅) were purchased from Absolute Standards INC, USA. These chemicals were used as received without further purification.

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Catalyst Characterization. Powder X-ray diffraction (XRD) pattern of Pd-samples were collected at room temperature using a Bruker D8 Advance X-ray diffractometer equipped with a monochromatized Cu K α radiation ($\lambda = 1.54055$ Å) source operating at 45 V and 40 mA. Surface measurements were carried out on a Micromeritics ASAP 2020 surface area analyzer using N₂ gas physisorption technique after degassing the samples overnight at 80 °C. Pulse CO chemisorption after reduction in H₂ was performed on an Altamira AM-200ip instrument. Before CO chemisorption, the sample was first heated at 120 °C and then cooled down to 30 °C. Subsequently, the sample was reduced with H₂ at 300 °C by ramping the temperature at a heating rate of 5 °C/min and then holding the temperature for 2 h. Pulses of CO in a He carrier gas were injected at 30 °C. The signal was monitored by a thermal conductivity detector (TCD). TEM images of the catalyst samples were collected on a JEM-2010F (Keck CAMM) aberration corrected transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV. Samples for TEM images were prepared by applying one drop of dilute suspension of the catalyst samples dispersed in acetone onto the carbon coated Cu grid and allowing the solvent to evaporate at room temperature.

Catalysis. All reactions were performed in a 50 mL stainless steel Parr reactor (model 4792HP/HT(FH) equipped with a thermocouple, pressure gauge, rupture disk and gas release valve. In a typical experiment, **1** (1.23 mmol), Pd_{10}/C (0.106 g, 0.1 mmol Pd), $Hf(OTf)_4$ (0.04 g, 0.05 mmol) and cyclohexane (25 mL) were loaded in the reactor. Subsequently, the reactor head was sealed, purged with ultra pure H_2 for three times and then pressurized to the desired pressure. The pressurized reactor was placed in a band heater connected to a heating controller and heated at 15 °C/min heating rate and held at desired reaction temperature for the set time. The solution was stirred at a constant rpm using a magnetic bar. Upon reaction, the reactor was cooled down in an ice bath and released the pressure. The reaction mass was transferred to a centrifuge tube to separate the solid catalyst by centrifugation. The supernatant liquid was decanted and used for GC-MS or GC analysis upon appropriate dilution with cyclohexane. Similar experimental procedure was followed to test furylmethanes **2-4**.

Product analysis. The conversion of precursors and the yields of alkanes and other oxygenated intermediates were determined on an Agilent 7890A GC connected to a MS Agilent 5977A MSD. A DB-5 column of dimension 30 m \times 250 μ m \times 0.25 μ m was used for analysis. The operating conditions of the GC-MS are as follows: injection volume 1.0 μ L, inlet temperature

250 °C, detector temperature 250 °C, and a split ratio 1:20. The initial column temperature was 40 °C (5 min) which was ramped at a rate of 15 °C/min and the final temperature was held at 320 $^{\circ}$ C for 10 min. Alkanes and other oxygenated intermediates were identified by their m/z numbers obtained from the mass hunter program and by comparing their retention times with standard samples. Actual concentrations of each identified products were quantified from their precalibrated plots of count numbers versus concentrations developed using standard alkane samples. HDO products of DMF and DMTHF were analyzed on a Shimadzu-GC-MS (model QP2010) and a GC (Agilent 7890A) equipped with an FID detector and HP-INNOWAX capillary column of dimension 0.25 μ m ID \times 250 μ m \times 30 m. The operating conditions of the GC are as follows: injection volume 1.0 µL, inlet temperature 250 °C, detector temperature 250 °C, and a split ratio of 1:10. The initial column temperature was 30 °C (hold time of 5 min) which was ramped at a rate of 15 °C/min and the final temperature was held at 250 °C for 5 min. Products were identified comparing their retention time with the retention time of the standard samples and by mass numbers from GC-MS analysis. Unless otherwise mentioned, the yields of alkanes and identified oxygenated intermediates were calculated on molar basis of total carbons. Total yield is the sum of all quantified alkanes and oxygenated intermediates.

$$Yield (mol\%) = \frac{Carbon yield of products (mol)}{Carbon of furylmethane (mol)} \times 100$$

Alkanes with less than 8 carbon numbers and some oxygenated intermediates were not identified, resulting in a loss of carbon balance.

Results and Discussion

Screening reaction conditions and promoters. Key steps in converting furylmethanes to the corresponding branched chain alkanes (Scheme 1) include hydrogenation, RO and deoxygenation of oxygenated RO intermediates. Mechanistic understanding of the sequence of these steps can make the process energy-efficient and improve the yield of alkanes of desired carbon numbers. To achieve this, we studied HDO of **1** using a physical mixture of Pd/C and a Lewis acidic metal triflate salt as a promoter. Metal triflate salts, $M(OTf)_3$, (M = L, Ce, Sm, Yb, Sc, Fe, Hf, Al) have been used to promote RO and oxygen removal of furans.^{15-16, 18} However, the exact role of the promoter remains elusive and contradictory. While one group found the ring-hydrogenated furan is a dead-end intermediate,¹⁵ another group¹⁶ reported furan ring

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hydrogenation occurs first before RO and oxygen removal by the triflate salt. We choose $Hf(OTf)_4$ as a promoter because of its high effective charge density at the metal center to facilitate RO by activating C-O linkages of furan rings of **1**.

First, we screened various reaction conditions (H_2 pressure, reaction time and temperature) with and without Hf(OTf)₄. Pd₁₀/C alone yields only 22% C₁₅H₃₂ and low carbon alkanes (C₁₄H₃₀, C₁₁H₂₄, C₉H₂₀) via C-C cracking. The total yield of all identified alkanes and fully furan ring saturated oxygenated intermediate ($C_{15}H_{25}O_3$, 6) is 53% (entry 2, Table 1). The addition of a small amount of $Hf(OTf)_4$ (0.05 mmol) results in significantly higher $C_{15}H_{32}$ (62%) and total alkane yields (95%; entry 7 of Table 1), with a very small amount of unconverted oxygenated intermediates and minimal C-C cracking (producing $C_{14}H_{30}$ as the only smaller alkane). A blank reaction without Pd/C and Hf(OTf)₄ shows no conversion of 1 (entry 1, Table 1). A reaction using half the amount of $Hf(OTf)_4$ (0.05 mmol) yields less alkanes (entry 8). A two-stage heating experiment with Pd₁₀/C-Hf(OTf)₄ (1st stage at 50 °C for 15 h followed by 2nd stage at 180 °C for 20 h) improves C₁₅H₃₂ (47%) and total alkane yields (70%) with fewer C-C cracking products (entry 4, Table 1) when compared with one-stage experiment (180 °C for 24 h). The screening experiments (Table 1) suggest that the reaction at 225 °C offers the highest alkane yield and C₁₅H₃₂ selectivity and minimal unconverted intermediate oxygenates by overcoming the energy barrier for C-O bond cleavage.¹⁹ Our maximum operating temperature is still lower than those reported at higher temperatures for similar HDO reactions of substrates with branched carbon backbone.^{11,13,14} This reduction in temperature, and hence the minimization in C-C cracking, is possible because of efficient C-O cleavage and oxygen removal by the triflate salt. Noteworthy, our reaction temperature is comparable to those used for HDO of aldol condensation derived fuel precursors containing one furan ring in which linear alkanes or oxygenates were formed as products.^{15,16} Increasing H₂ pressure from 25 to 50 atm accelerated HDO of intermediate 6, resulting in increased yield of desired C₁₅ and C₁₄ alkanes (entries 5-7, Table 1).

Since the triflate salt can dissociate to triflic acid (HOTf) by water formed during HDO, we also used HOTf as a promoter. The results in Table 1 (entry 9) reveal that HOTf promotes $C_{15}H_{32}$ (35%) and $C_{14}H_{30}$ (20%) yields when compared with Pd_{10}/C alone because of proton assisted RO of furan moieties of **1**. Another reaction using 4 equivalent of HOTf, maximum



 Pd_{10}/C and promoters were physically mixed. ^aNo Pd_{10}/C . ^bTwo staged heating – 1st stage at 50 °C for 15 h and 2nd stage at 180 °C for 20 h. ^cHf(OTf)₄ = 0.025 mmol. ^dHOTf = 0.05 mmol. Other reaction conditions: Hf(OTf)₄ (0.040 mg; 0.05 mmol), HOTf (7.5 mg, 0.05 mmol), HfCl₄ (0.015 g, 0.05 mmol), HfO₂ (0.010 g, 0.05 mmol), H-BEA-25 (0.050 g), cyclohexane (25 mL), 24 h.

amount of HOTf could be formed from complete dissociation of one equivalent of Hf(OTf)₄, the yield of jet fuel ranged alkanes improved slightly (entry 10, Table 1) than the reaction using 1 equivalent HOTf. However, HOTf is not as effective as triflate salt in total alkane yields and C_{15} alkane selectivity, indicating that the Lewis acidic metal center of Hf(OTf)₄ predominantly catalyzes the C-O cleavage of the furan rings. Heterogeneous acidic zeolite (HBEA-25) performed worse than the homogeneous acid due to potentially lower accessibility of the acid sites in its micropores by the bulky molecules **1**; importantly, the zeolite promotes significant C-C cracking. Another Lewis acidic Hf salt, HfCl₄, formed much less $C_{15}H_{32}$ (15%) and $C_{14}H_{30}$ (11%) products than those obtained with Hf(OTf)₄ or acid (HOTf, HBEA-25) promoters, and the majority of intermediate oxygenate, **6**, remained unconverted (32%). This suggests that HfCl₄ could not activate C-O bonds of furan rings through its binding with 'O', presumably due to its poor Lewis acidity in cyclohexane or poor dissociation to generate Brønsted acid (HCl) in water formed during HDO. Similarly, HfO₂ also could not promote HDO, leading to a significant amount of **6** (28%).

Noteworthy, Hf(OTf)₄ is the most effective among the promoters tested because of its unique characteristics. It contains four strong electron withdrawing triflate ligands (OTf = -OSO₃CF₃) with three fluorine atoms in each ligand that makes the Hf center highly electron deficient and strongly Lewis acidic, with strong affinity to bind the nucleophilic 'O' of -C-O linkages of furan moieties; it thus activates the etheric 'O' towards RO (Scheme 2). Further, 'O' atoms of sulfonate group (-SO₃) of triflate ligand could facilitate cleavage of β-C-H bond through formation of an intermediate (species B) and accelerate RO of Hf-bonded ether to Hf-bonded alcohol (species C). Marks et al. have shown a similar pathway for opening of C-O linkages of 5-and 6-members hydrogenated rings with Hf(OTf)₄.^{18a}



Scheme 2. $Hf(OTf)_4$ assisted ring opening (RO) of hydrogenated furan ring oxygenate 6. F and MF are furan and 2-methylfuran, respectively.

Next we studied the effect of Pd loading by varying the molar ratios of **1** to Pd. These experiments at **1**:Pd molar ratios of 12 - 44 reveals that the maximum yield of C_{15} alkane is achieved at the molar ratio of 12 (Figure 1a). A gradual decrease in C_{15} alkane yield with high accumulation of unconverted oxygenate **6** is observed with decreasing Pd amount. In addition, several other oxygenate intermediates remain undetected, contributing to carbon loss at low Pd amount.

Upon optimization of reaction temperature (225 °C), H₂ pressure and Pd amount (1:Pd $(Pd_{10}/C) = 12)$, we varied the reaction time from 5 h to 24 h (Figure 1b). Intermediate **6** is formed as the major product in 5 h with total detected carbon yield of little over 80%. This intermediate is fully converted to C₁₅ and C₁₄ alkanes after prolonged reaction (24 h). Interestingly, the total detected carbon yield for 24 h reaction is much higher than that of 5 h reaction. This suggests that the product solution in 5 h reaction contained some undetected oxygenates (Figure 2 shows peaks for undetected oxygenates between RT 16-18 min in GC chromatogram) that are also converted to alkanes at long times.



Figure 1. Hydrodeoxygenation (HDO) results of compound **1** with Pd_{10}/C -Hf(OTf)₄ at different (a) molar ratios of **1** to Pd and (b) reaction time. Reaction conditions: **1** (0.300 g; 1.23 mmol), Hf(OTf)₄ (0.05 mmol), H₂ (50 atm), cyclohexane (25 mL), 225 °C. Pd amount was varied from 0.028 mmol to 0.1 mmol. Exact amount of Pd₁₀/C used for **1**:Pd variation experiment are in the supporting information (Table S1). Table S2 shows data used in Figure b. Reaction time for **1**:Pd experiments is 24 h.

Time Profile of HDO with and without $Hf(OTf)_4$. To understand what happens in the early stage of the reaction pathway towards alkane formation, especially ring hydrogenation, RO and oxygen removal, we investigate the reaction profile at early stages at room temperature (25 °C) and at 225 °C. The reactor was quenched at specific times in an ice-bath and the solution was analyzed by GC-MS. First, **1**, catalyst (Pd₁₀/C-Hf(OTf)₄) and solvent were added in the reactor, stirred the mixture for 10 min without pressurizing the reactor with H₂. The chromatogram in Figure 2 shows a single peak for **1**, indicating no reaction occurs without H₂. Then we purged the reactor with ultrapure H₂ for three times and hold the pressure at 50 atm and 25 °C for 10 min with continuous stirring. Two new peaks appear, corresponding to intermediate **6** and a partially furan ring hydrogenated oxygenated intermediate **5**. This result indicates that hydrogenation of furan ring is facile at 25 °C.

RO of **6** to ring-opened oxygenate (**7**), alkanes and other unidentified products occurred during heating to 225 °C (heating rate 15 °C/min). A significant amount of **7** with a small amount of alkanes formation during heating indicates that RO of **6** to **7** is fast. RO step is depicted in Scheme 2. At long times, C_{15} and C_{14} alkanes form via deoxygenation, dehydrogenative decarbonylation and hydrogenation, along with small amounts of C_9 - C_{11} alkanes via C-C cracking. Intermediates with di or tri hydroxyl groups are also expected to form from **7** via opening of two other furan rings (Scheme 3). However, the latter two oxygenates were not identified, possibly due to their faster conversion to alkanes as they are formed from **7**. Notably, the GC chromatogram after 24 h reaction shows fewer, small peaks for unidentified species, accounting for a small loss in carbon balance (3%), compared to shorter times (e.g., 5 h). The corresponding reaction profile showing yields of various products as a function of time is shown in Figure S1.



Figure 2. GC chromatograms obtained during HDO of **1** with $Pd_{10}/C-Hf(OTf)_4$; major compounds and retention times on the right. Reaction conditions: **1** (0.300 g; 1.23 mmol), $Hf(OTf)_4$ (0.05 mmol), H_2 (50 atm), cyclohexane (25 mL), temperature and time as indicated in the graph. 0 h is the time when the temperature of the reaction mixture reached 225 °C. The heating rate is 15 °C/min.

In the absence of Hf(OTf)₄, ring hydrogenation of **1** to **6** follows a similar trend but RO of **6** to **7** is not evident at 225 °C, even after 1 h of reaction at 225 °C (Figure S2). In contrast, two unidentified peaks are observed at slightly higher retention times of **6**. Thus, the RO pathway without Hf(OTf)₄ is significantly different from that observed with Hf(OTf)₄. In the latter case, facile RO of **5** to **7** and subsequent HDO of **7** to alkanes occur at 225 °C. This difference in results with and without Hf(OTf)₄ further confirms significant roles of the promoter in RO. Prolonged reaction (24 h) without the promoter at 225 °C shows peaks for alkanes (entry 2, Table 1) and several unidentified peaks for oxygenates, which were not observed in the reaction with Hf(OTf)₄, and account for higher carbon loss (37%).

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Reaction pathway and network. A possible reaction network is proposed in Scheme 3. First, hydrogenation of furan rings of **1** over Pd catalyst gives the fully ring hydrogenated intermediate 6. Second, RO of 6 to 7 occurs through formation of an adduct between strong Lewis acidic Hf center of Hf(OTf)₄ and the 'O' of the furan ring and concurrent elimination of a H at the β carbon of the 'O'. Subsequent C–O cleavage forms a hydroxyl intermediate with an olefinic C=C group, consistent with the prior work.^{18a} A controlled experiment using lower H₂ pressure (6 atm) reveals the formation of 7 is independent on the H_2 pressure (Figure S3), which strengthens our proposition of β -H elimination during ring-opening. Two other ring saturated furans of 7 are also expected to be similarly opened to hydroxylated intermediates (8). Third, cleavage of Hf-bonded hydroxylated intermediate to Hf-H₂O and concurrent hydrogenation of intermediate forms C_{15} alkane. Fourth, we observed formation of a significant amount of C_{14} alkane, which can be explained by dehydrogenative decarbonylation of primary alcohol moiety of 7. Dehydrogenative decarbonylation of primary alcohols such as benzyl alcohol and HMF on Pd catalysts ^{20a, 20b} and butanol over Pt, Ru catalysts^{20c} have been reported. Proposed pathway for dehydrogenative decarbonylation of benzyl alcohol involved adsorption of primary alcohol moiety of benzyl alcohol (-CH₂OH) onto the Pd(111) surface, followed by dehydrogenation of the alcohol to an aldehyde and finally decarbonylation of derived aldehyde. Both dehydrogenative decarbonylation^{20a} and decarbonylation^{20c} can occur on the Pd surface. In analogy to benzyl alcohol conversion, we propose the primary alcohol group of a portion of intermediate 7 is dehydrogenated an intermediate 9, which is subsequently converted to intermediate 10 via RO of the two remaining furan rings, similar to formation of intermediate 8. Intermediate 10 is then decarbonylated to C_{14} alkane as shown in Scheme 3. Noteworthy, RO of two other methyl substituted furan rings will form secondary alcohols, which are unable to decarbonylate via dehydrogenation like the primary alcohol. We believe C-C cracking of furan rings at tertiary carbon of intermediate 8 also occurs, which forms intermediates (oxygenated or alkenes (11 and 12)) for C_{10} and C_{11} alkanes. Alkenes are hydrogenated over Pd/C to the corresponding alkanes. C₉ and other smaller alkanes could form from C-C cracking of high carbon alkanes.



Scheme 3. Possible reaction network for conversion of 1 to alkanes using $Pd/C-Hf(OTf)_4$ catalyst.

Probing reaction pathway using single furan molecules. To further elucidate the mechanism over Pd/C-Hf(OTf)₄ catalyst, we use simple surrogates of **1** such as DMF and DMTHF. A recent study describes full ring hydrogenation of DMF over a Pd/C catalyst without RO,²¹ consistent with the findings of Sutton et al.¹⁵ RO of unsaturated furan over a Pt/C catalyst was observed, which parallels with computational and experimental work on RO of substituted (-CHO, -CH₂OH, no side group) single furan ring molecules over a Ir(111) single crystal catalyst. In the latter case, the RO paths depend on the degree of ring saturation and the electonegativity of the side-chain functional groups.²² DMF conversion over Pt/C and bimetallic PtCo/C (Pt₃Co/C and Pt₃Co₂/C) catalysts showed²³ that DMF hydrogenation to DMTHF and RO to 2-hexanone, 2-hexanol, 2-propoxyhexane and hexane are facile over Pt/C due to strong chemisorption of furans on the surface. Monolayer oxide (Co₃O₂) of Pt₃Co₂/C caused weaker interaction of furans on the surface, resulting in lower DMF conversion. Pt₃Co exhibited intermediate catalytic activity. These results suggested furan RO occur via ring hydrogenation upon accessing exposed metal surface. Another study reported RO of DMF over Ru/C occurs via parallel pathways in which both partial saturated and fully saturated furan rings opened,²⁴ an observation supported

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by DFT calculations and microkinetic modeling. Catalytic conversions of furfural and HMF to low carbon alkanes involving hydrogenation of C=O bonds and furan-rings and C-O hydrogenolysis have also been reported.²⁵

We observe that the DMF conversion follows a similar pathway as 1 with $Pd_{10}C$ -Hf(OTf)₄ leading to hexane as the major product (Figure 3A). First, DMF undergoes rapid hydrogenation to DMTHF and partially ring hydrogenated DMF-H₂ at 25 °C and 50 atm H₂ with full conversion of DMF (Scheme 4). A significant fraction of hexane forms during heating the reaction mixture to 225 °C at 50 atm H₂. Both fully hydrogenated and partially hydrogenated furans could undergo RO by Hf(OTf)₄ during heating as the GC peak intensity of both species decreased, although RO of partial ring-saturated furan is believed to be faster as per energy calculation reported previously.²² The remaining furans (partially and fully saturated) quantitatively convert to hexane in significantly shorter time (1 h) than that of multi-furans furylmethane 1 (24 h) and with much cleaner chromatogram. Unlike furylmethane, ring-opened hydroxylated intermediate was not observed for DMF. This could be attributed to the faster cleavage of the -C-OH---Hf linkage of the hydroxylated species (Scheme 2). Comparison of furylmethane conversion with its surrogate molecule suggests that Hf(OTf)₄ is much more effective and selective for RO of partially or fully hydrogenated furan of a single ring (DMF). This may be due to steric hindrance for stable adduct formation between Hf^{4+} , furan 'O' and -OSO₃CF₃ groups by the bulky furylmethane molecule as shown in Scheme 2.

A room temperature reaction of DMF with Pd_{10}/C alone shows formation of only DMTHF and DMF-H₂ in 2 h at 25 °C and 50 atm H₂. RO and deoxygenation start upon addition of Hf(OTf)₄ and heating the reaction mixture to 225 °C (Figure 3B). Similarly, DMTHF is the main product from DMF at high temperature (225 °C) without Hf(OTf)₄ in 1 h (Figure S4). The RO step starts only after addition of Hf(OTf)₄ into the resulting DMTHF leading to formation of hexane. This result further illustrates that Hf(OTf)₄ is necessary to open fully hydrogenated ring.



Figure 3. (**A**) GC chromatograms obtained during HDO of DMF with Pd_{10}/C -Hf(OTf)₄: (a) without H₂, (b) with H₂ added at 25 °C after 10 min, (c) after the reaction mixture reached to 225 °C, and (d) after reaction for 1 h at 225 °C. Other conditions: Pd_{10}/C (106 mg; 0.1 mmol), Hf(OTf)₄ (0.040 g; 0.05 mmol), DMF (0.118 g, 1.23 mmol), cyclohexane (10 mL), 50 atm H₂. (**B**) GC chromatograms obtained during HDO of DMF (0.123 g, 1.23 mmol) with Pd_{10}/C (0.106 g, 0.1 mmol Pd) in the absence of Hf(OTf)₄: (a) without H₂, (b) with H₂ added at 25 °C after 40 min, (c) after 1 h, (d) after 2 h and (e) after addition of Hf(OTf)₄ (0.040 g, 0.05 mmol) and heating to 225 °C in cyclohexane (10 mL). DMF-H₂, *trans*- and *cis*-DMTHF and hexane have the same RT in all chromatograms.



Scheme 4. Dimethylfuran conversion with and without Hf(OTf)₄.

Effect of furylmethane structure on alkane selectivity. We found C-C cracking of oxygenated intermediate of **1** caused some selectivity loss of desired $C_{15}H_{32}$ product. It is hypothesized that

C-C cracking can be minimized by tuning molecular structures of furylmethanes with tailored carbon-chain, furan numbers and the carbon center. Answers to this hypothesis will be critical in designing and developing appropriate fuel precursors for selective production of high carbon branched chain alkanes. In addition to **1**, we choose three more furylmethanes (**2**, **3** and **4**; Scheme 1) with different numbers of furan rings and nature of carbon center (tertiary *versus* quaternary) for the comparative study. These furylmethanes were subjected to react with Pd_{10}/C - $Hf(OTf)_4$ at the optimal reaction conditions developed for **1** (entry 7, Table 1). Figure 4 compares the products distribution of alkanes at the full furylmethanes' conversion. C_{14} furylmethane (**2**) with two furan rings and a butane chain yields the corresponding C_{14} alkane with the highest selectivity (92% yield). Precursor **4**, C_{21} furylmethane with four furan rings, yields 60% C_{20} alkane out of total detected carbon yield of 63%, indicating that the larger molecule with several furan rings and a quaternary carbon gives more C-C cracked alkanes than **4** with alkane yield of maximum carbon number (C_{13}) of 52%. Figure 4 suggests that



Figure 4. Yields of alkanes during HDO of different furylmethanes over Pd_{10}/C -Hf(OTf)₄. Reaction conditions: Pd_{10}/C (106 mg; 0.1 mmol), Hf(OTf)₄ (0.040 g; 0.05 mmol), furylmethanes (1.23 mmol), cyclohexane (25 mL), 50 atm H₂, 225 °C, 24 h. Table S3 tabulates the raw data.

furylmethanes with fewer furan rings and a straight carbon-chain unit are beneficial to produce alkanes with high selectivity, e.g., **2**. In contrast, precursors with multiple furan rings possibly

form many ring-opened oxygenates, from which multiple C-C cracking reactions could occur during deoxygenation. Another important observation is that 1 forms significant amount of alkane with one carbon less than its parent molecule, which was not observed for other furylmethanes. This can be explained by the presence of one un-substituted furan in 1, which forms a primary alcohol

upon RO and undergoes dehydrogenative decarbonylation to C_{14} alkane. Other furylmethanes containing methyl substituted furan rings in their molecular structure will form secondary alcohols upon RO and render their dehydrogenative decarbonylation to alkanes with one carbon less than their parent molecules.

Comparative analysis. A comparative analysis of C_{12} - C_{21} furylmethanes HDO to alkanes with $Pd/C-Hf(OTf)_4$ and other reported catalysts is presented in Table 2. It shows the yield of alkanes depends on the reaction conditions and the nature of the catalysts. A Pt catalyst containing mixed Al_2O_3 and carbon supports achieved low alkane yield (68%) from C_{14} furylmethane at high temperature (350 °C; entry 2).^{6a} At the same temperature, C₁₅ furylmethane over the Pt catalysts on acidic Al₂O₃ and weakly acidic TiO₂ supports, along with Pt/C, yielded slightly higher alkanes (85%; entries 1 and 3). In contrast, the Pd/C-Hf(OTf)₄ catalyst in our study yields much higher alkanes (94-97%) from both C_{14} and C_{15} furylmethanes at lower temperature (entries 8-9). A Eu(OTf)₃-Pd/C catalyst has also achieved high alkane yield from C₁₂ furylmethane, indicating the triflate salt is beneficial for RO.²⁶ A Pd/NbOPO₄ catalyst gave similar C₁₅ alkane yield (84% $C_{15}H_{32}$, entry 6) as the Pt catalysts over alumina and titania supports from C_{15} furylmethane.^{14b} Notably, the Pd/NbOPO₄ catalysis was conducted at considerably mild temperature like us. NbO_x species activated the C-O RO of furans, consisting with a prior report,²⁷ and Brønsted acidic phosphate sites promoted the dehydration step. Another NbOPO₄ catalyst with weaker hydrogenation metal (Ru) gave much less C₁₅H₃₂ (26%) and total alkanes (67%),^{14b} indicating hydrogenation activity of the metal is important for ring hydrogenation and post-hydrogenation of RO intermediates. For the same reason, Ni/NbOPO₄ catalyst produced only 16% jet fuel ranged alkanes (entry 8). In another work, a Ni catalyst over ZSM-5 support achieved higher C₁₅ alkane (50%) owing to higher reaction temperature (260 °C), higher H₂ pressure (60 atm) and mesoporous zeolite support (entry 9).²⁸ The authors found that higher Ni dispersion on the ZSM-

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Entry	C numbers of furylmethane	Catalysts	T (°C)	t (h)	Solvents	<i>P</i> _{H2} (atm)	Conv. (%)	Alkane yield	Reference
1	C15	Pt/C-TiO ₂	350	_a	-	50	>99	85	11
2	C14	Pt/C-Al ₂ O ₃	350	_a	-	50	>99	94	11
3	C15	Pt/C-Al ₂ O ₃	350	_a	-	50	>99	85	11
4	C14	Pd/C (3%Pd)	350	_a	-	50	>99	20	11
5	C12	Pd/C- Eu(OTf) ₃	200	16	EtOAc	40	>99	98	26
6	C15	Pd/NbOPO ₄	200	12	cyclohexane	40	100	99	14b
7	C15	Ru/NbOPO ₄	200	12	cyclohexane	40	>99	67	14b
8	C15	Ni/NbOPO ₄	200	12	cyclohexane	40	>99	16	14b
9	C15	Ni/H-ZSM-5	260	_ ^a	-	60	>50	50	28
10	C15	Ni/H-ZSM-5- FG	260	_a	-	60	>99	70	28
11	C15	Pd/C-Hf(OTf) ₄	225	24	cyclohexane	50	>99	97	This work
12	C14	Pd/C-Hf(OTf) ₄	225	24	cyclohexane	50	>99	94	This work
13	C13	Pd/C-Hf(OTf) ₄	225	24	cyclohexane	50	>99	75	This work
14	C21	Pd/C-Hf(OTf) ₄	225	24	cyclohexane	50	>99	62	This work

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^areactions in a flow reactor. EG = Ethylene glycol.

5 support via ethylene glycol (EG) assisted synthesis of the catalyst enhanced C_{15} alkane yield to 70% (entry 10).²⁸

Conclusions

We demonstrated that commercial Pd_{10}/C catalyst with a small amount of $Hf(OTf)_4$ promoter is effective for conversion of C_{13} - C_{21} furylmethane oxygenates to the corresponding branched chain alkanes with high yield. The reaction occurs at considerably lower temperature because of facile ring-opening of furan units by strong Lewis acidic Hf center of the promoter. Time profile and controlled experiments depict that the reaction progresses sequentially via furan ring hydrogenation, ring-opening, deoxygenation and hydrogenation pathways. Hf(OTf)₄ facilitates ring-opening of furan via formation of an adduct between Hf⁴⁺ and nucelophilic 'O' of the ring and activating -C-O linkages. 'O' atoms of sulfonate group (-SO₃) of triflate ligand likely facilitate cleavage of β C-H bond through formation of a cyclic intermediate and accelerate the ring-opening of Hf⁴⁺-bonded ether to Hf⁴⁺-bonded hydroxyl intermediates. Subsequent cleavage of -C-OH linkages of -C-OH…Hf⁴⁺ adduct and hydrogenation of intermediates form branched alkanes. The intermediate with primary alcohol also undergoes dehydrogenative decarbonylation reaction to alkane. Probe reactions with single furan ring surrogate molecules suggest that the reaction is faster for single ring molecules than the multi-ring furylmethanes and $Hf(OTf)_4$ is necessary for ring-opening. An optimal reaction condition achieves 97% yield of jet fuel ranged alkanes with 93% selectivity in C₁₅H₃₂ and C₁₄H₃₀.

Acknowledgements

This work is conducted with financial support as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001004. Authors acknowledge Professor Dion Vlachos, Catalysis Center for Energy Innovation, University of Delaware for his valuable time providing helpful technical suggestions and feedback on the manuscript.

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Electronic supplementary material (ESI). HDO experimental results at varying Pd_{10}/C :1 molar ratio and reaction time, carbon-chain-length of substrates, reaction profile and GC chromatograms.

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