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One-step production of long-chain hydrocarbons from waste-biomass-derived chemicals using bi-functional heterogeneous catalysts

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In this study, we demonstrate the production of long-chain hydrocarbons (C_{8+}) from 2-methylfuran (2MF) and butanal in a single step reactive process by utilizing a bi-functional catalyst with both acid and metallic sites. Our approach utilizes a solid acid for the hydroalkylation function and as a support as well as a transition metal as hydrodeoxygenation catalyst. A series of solid acids was screened, among which MCM-41 demonstrated the best combination of activity and stability. Platinum nanoparticles were then incorporated into the MCM-41. The Pt/MCM-41 catalyst showed 96% yield for C_{8+} hydrocarbons and the catalytic performance was stable over four reaction cycles of 20 hour each. The reaction pathways for the production of long-chain hydrocarbons is probed with a combination of infrared spectroscopy and steady-state reaction experiments. It is proposed that 2MF and butanal go through hydroalkylation first on the acid site followed by hydrodeoxygenation to produce the hydrocarbon fuels.

1 Introduction

Liquid petroleum fuels are responsible for more than 93% of all transportation energy consumption in the United States, and volatility in gas prices, reduced reserves and greenhouse gas emissions have led to a rapidly growing interest in biofuels.^{1–3} The conversion of biomass to drop-in transportation fuels offers the benefit of providing a renewable replacement for hydrocarbon fuels currently used in a vital subset of transportation (*i.e.*, heavy transport applications).^{4,5} It has also been proposed to be a method of reducing overall CO_2 emissions by closing the carbon cycle.⁶ A substantial disadvantage to the use of biomass, however, is the competition with resources for food production, and thus recent research has focused on converting residual bio-waste into transportation fuels.⁷

Unfortunately, biomass stores solar energy in the form of C–H and C–C bonds along with energy-neutral C–O and O–H bonds. To harness the energy contained in biomass, the C–O and O–H bonds should be removed while preserving the C–H and C–C bonds with maximum overall energy efficiency. Three major approaches to the conversion of biomass are currently available: gasification, pyrolysis, and hydrolysis.⁸ Gasification involves the complete breakdown of the carbohydrate biomass into CO and H_2 by dissociating all the C–C and C–H bonds and most O–H bonds. The C–C and C–H bonds are then reformed

via Fischer–Tropsch synthesis, resulting in a loss of 50–60% of the heat content in the biomass.⁹ Pyrolysis is a somewhat less energy intensive process, during which C–O and O–H bonds are dissociated.^{10–12} However, some of the C–C and C–H bonds in the biomass are also broken during pyrolysis; this leads to the semi-selective production of liquid fuels and a loss of about 45% loss of the heat from the biomass.^{10–12} By comparison, hydrolysis provide higher energy efficiency due its inherently milder and selective conversion. However, a series of lengthy and complicated reaction steps are typically necessary generate biofuels from biomass,⁸ because biomass is mainly composed of cellulose and lignin, both polymerized sugars. First, the cellulose biomass must undergo complete C–O bond dissociation for de-polymerization into glucoses. Then, the glucoses must be further dehydrated or isomerized to a wide spectrum of platform chemicals,^{8,13–16} among which 2-methylfuran (2MF) and butanal have recently attracted interests.^{17–19}

Recent research by Corma *et al.* has demonstrated a promising multi-step technique for producing long-chain hydrocarbons from 2-methylfuran (2MF) and butanal with high activity.²⁰ First, Amberlyst-15 is used as an acid catalyst in a liquid-phase batch reaction to hydroalkylate 2MF with butanal into 1,1-bisylvl-alkanes, which are then separated from 2MF, butanal and water (side product). This intermediate product is then hydrodeoxygenated over Pt in a separate flow reactor to produce long-chain hydrocarbons. The process minimizes unnecessary C–C and C–H bond dissociation, and thus has high energy- and carbon-efficiency. However, the non-continuous combination of a batch reactor with a plug flow reactor reduces the throughput

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Scheme 1 Scheme of C_{8+} production bi-functional Pt/MCM-41 catalyst.

of the approach and makes scale-up challenging. Furthermore, extra energy and time are required for the separation of 1,1-bisylalkanes from 2MF and water.

Combining these process steps into a single, continuous reaction procedure would increase not only the energy efficiency, but also the rate of production towards long-chain hydrocarbons. Herein, we demonstrate novel bi-functional catalysts (Pt/MCM-41) for producing long-chain hydrocarbons (C_{8+}) by combining solid acid and hydrodeoxygenation (HDO) functionalities, as shown in Scheme 1. The catalytic activity of the bi-functional catalyst is tested in a fixed bed reactor, and the reaction mechanism is probed with *in situ* infrared spectroscopy and steady-state kinetic experiments.

2 Experimental

2-Methylfuran (2MF) (98%), butanal (98%), MCM-41 mesostructured aluminosilicate (Si/Al ratio of 40), ammonium tetrachloroplatinate(II) (99%), methanol (99.8%), and Amberlyst-15 (hydrogen form), were purchased from Sigma-Aldrich, and used as-received. ZSM-5 (Si/Al ratio of 80) was purchased from Alfa Aesar, and was also used as received. Ultra high purity hydrogen (99.999%) was purchased from Airgas.

2.1 Catalyst synthesis

The 0.1 wt% Pt/MCM-41 catalyst used in this work was prepared by incipient wetness impregnation of MCM-41 with a methanol solution of ammonium tetrachloroplatinate.²¹ The MCM-41 was mixed with the platinum solution under constant stirring at room temperature and the methanol naturally evaporated overnight. The mixture was then dried in an oven at 373 K for 10 h, and calcined at 823 K for 3 h with temperature ramping from room temperature to 823 K at the rate of 5 K min⁻¹.

2.2 Catalyst characterizations

X-ray powder diffraction (XRD) patterns of the MCM-41 and Pt/MCM-41 were obtained with a Rigaku Miniflex II X-ray powder diffractometer equipped with a Cu K α X-ray source. The specific surface area of the catalyst and nitrogen adsorption and desorption isotherms were measured with a Micromeritics ASAP 2020 surface area and porosimetry analyzer. Before each test, the samples were degassed at 383 K for 3 h under vacuum. Pore size distributions were calculated using the Barret–Joyner–Hollenda (BJH) method based on the nitrogen adsorption data. The morphology of the samples was characterized with a Hitachi H800 transmission electron microscope (TEM), with an acceleration voltage of 200 kV. The nanoparticles were dispersed in acetone onto carbon film copper TEM grids. The X-ray photoelectron spectroscopy (XPS) spectra were measured on Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K α (1486.6 eV) as X-ray source operated at 15 keV and 120 W. The pass energy was fixed at 40 eV for the detailed scans. The binding energy in the XPS spectra is calibrated with carbon signal (C1s at 284.8 eV).

2.3 Catalytic activity and stability tests

Catalytic screening was performed in two distinct sets of experiments. The first set used a standard batch reactor set-up to screen for solid materials that would make effective HA catalysts, and involved a broad sampling of potential solid-acid catalysts. The reactions were performed at moderate temperatures to set a baseline for HA activity. A 15 mL mixture of 2MF and butanal (mol ratio of 2MF:butanal is 2:1) was added to 0.22 g of catalyst. Then the mixture was heated to 333 K and magnetically stirred for 20 h. After the reaction, the liquid product was filtered out and analyzed with a gas chromatography-mass spectrometer (GC-MS). In the GC-MS, the liquid products are vaporized at 523 K and separated with RTX-5 column. After going through the GC column, the products are detected by both flame ionization detector (FID) and quadrupole mass spectrometer (Finnigan TSQ MS).

The second set of reactions was performed in a plug-flow reactor to validate the generation of C_{8+} on the bi-functional catalysts. The effect reaction temperature on the C_{8+} production was further explored over a larger temperature window, and the long-term stability of the bi-functional catalysts was tested by running C_{8+} production on the same bi-functional catalyst for multiple times without catalyst regeneration. A stainless-steel fixed bed reactor with outer diameter of 12.7 mm and inner diameter of 9.5 mm was used. The catalyst (4.8 g) was loaded in powder form without pelletizing, and was supported by a quartz wool plug in the reactor. Before reaction, the catalyst was activated under hydrogen flow of 60 mL min⁻¹ at 673 K and 3.5 MPa for 1 h. The reactor pressure was controlled by a backpressure valve (GO Regulator, BP-60), and measured with a pressure gauge. After the activation, the system was cooled down to the desired reaction temperature (between 503–623 K), and a mixture of 2MF and butanal (molar ratio of 2MF:butanal of 1:1 with total weight of 19 g) was pumped into the system by a high performance liquid chromatography (HPLC) pump with a flow rate of 0.02 mL min⁻¹, under the same hydrogen flow rate and pressure as in the

activation step. The mixing of the hydrogen gas and liquid mixture was done just prior to entering the reactor. The reaction was run continuously for 20 h and the products were collected during that period in a liquid–gas separator (kept at 277 K) after the reactor. Typically, more than 85% of the injected 2MF and butanal were converted to liquid phase products. Approximately 17 g of liquid phase was obtained after the reaction with about 20% being aqueous and the balance present as organics. The organic phase was analyzed using GC-MS.

2.4 *In situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

The *in situ* DRIFT spectra were acquired on a Bruker Equinox 55 spectrometer coupled with a DRIFT cell (Harrick Scientific Praying Mantis) and a DTGS detector. A 0.1 wt% Pt/MCM-41 sample was first degassed at 573 K for 2 h under 50 mL min^{−1} He flow and atmospheric pressure. The cell was then cooled down to 333 K under flowing He. A background with a spectral resolution of 4 cm^{−1} was collected after the temperature had stabilized by averaging over 640 scans. Then, the reaction mixture of 2-MF and butanal (mol ratio of 2MF:butanal is 1:1) was introduced into the DRIFT cell by a HPLC pump at the rate of 0.01 mL min^{−1}. The DRIFT spectra were obtained using the same collection parameters as the background.

3 Results and discussion

Various solid acids were first tested in the batch reactor for the 2MF and butanal alkylation to produce 1,1-bis(2-methylbutyl)butane, and the catalytic activities were compared based on the conversion of 2MF. ZSM-5 zeolite was chosen based on its well-known acid catalysis properties,^{22,23} including alkylation.²⁴ However, ZSM-5 shows poor activity for the alkylation between 2MF and butanal, with only 1 ± 1% of 2MF converted after 20 h of reaction. The low activity of ZSM-5 may be attributed to the 10 member rings with the zeolite pore size in the range of 5.4–5.6 Å being too small to permit 2MF access to the acid sites.²⁵ The molecular size of 2MF is estimated to be between 4.8–7.3 Å, based on literature reports.^{26,27} An attempt was made to increase the accessible surface area by synthesizing mesoporous ZSM-5 following literature.²⁸ This, however, resulted in only a slight increase in the catalytic activity for 2MF and butanal alkylation from 1% to 4%.

In the case of solid acid catalysts with more accessible acid sites (MCM-41, sulfated zirconia, and Amberlyst-15), substantially higher activity (above 60%) toward 2MF conversion was observed, with Amberlyst-15 showing the highest conversion of the group. Sulfated zirconia, however, was not chosen for further study because the sulfate group on the sulfated zirconia may deactivate HDO-active metals, such as Pt,²⁹ and may lead to sulfur contamination of the final products. Likewise, Amberlyst-15 was not selected for further study as it is a styrene-based resin, and is only stable up to temperatures of ~423 K,³⁰ which is on the low end of the temperature range required for HDO (473–673 K).³¹ Aluminosilicate MCM-41, on the other hand, was reported to have excellent thermal stability and is unlikely to poison the

metal HDO catalysts.^{32,33} Further, compared to ZSM-5, the MCM-41 with (Si/Al ratio of 40) exhibits much larger pores (2.6 ± 0.3 nm), more accessible surface area (650 ± 5 m² g^{−1}), and also higher activity (62 ± 5% 2MF conversion) for the acid catalyzed 2MF and butanal alkylation. Therefore, MCM-41 was chosen to serve as the acid catalyst for further studies and as the support of the HDO functionality for the bi-functional catalysts.

On the MCM-41, Pt is introduced by conventional wet impregnation methods as the HDO function entity for the bi-functional catalysts, as Pt has been used for many HDO processes.^{34,35} As shown in the bright field TEM images in Fig. 2a, the Pt nanoparticles appear darker due to the higher electron density of Pt than that of silica and alumina in the wall of MCM-41, which are the gray stripes apparent in the Fig. 2a. The Pt nanoparticles grow within the boundary of the MCM-41 pores, and the growth direction of Pt nanoparticles aligns with the pore channels of MCM-41. Thus, based on the TEM images, the Pt nanoparticles are believed to be located inside the pores of the MCM-41 instead of on the outer surface of the MCM-41. As Pt and MCM-41 are the two functional entities for the bi-functional catalyst, having the Pt nanoparticles distributed inside the pores of the MCM-41 could facilitate the C₈₊ production by decreasing the spatial separation between the two reaction steps, as shown in Scheme 1.

To be active for HDO, the Pt should be in the metallic form.^{21,22} The oxidation state of the Pt after reduction under H₂ at 400 °C was characterized with X-ray photoelectron spectroscopy (XPS). As seen from the Pt 4f XPS profile, the binding energy of Pt 4f 5/2 (70.6 eV) is consistent with that of metallic Pt.³⁶ Thus, both TEM and XPS results demonstrate that Pt is not only introduced on the MCM-41, but is also present in the metallic phase needed for the HDO reaction.

Metallic Pt is one of the two components needed for the bi-functionality, the other part being the MCM-41 support supplying acid sites for the alkylation reaction between 2MF and butanal. For such activity, the mesopore structure of the MCM-41 must be retained after introducing Pt for HA of the 2MF and butanal. The TEM image in Fig. 2a shows an ordered

Fig. 1 Conversion of 2-methylfuran on different solid acids catalyst for 20 h in the alkylation reactions between 2-methylfuran and butanal.

Fig. 2 (a) Bright field TEM images of Pt/MCM-41 and (b) Pt 4f XPS profile of H_2 reduced Pt/MCM-41.

pore system with pore size in the range of 2–3 nm, similar to that of the fresh MCM-41, and suggests that the mesopore system of Pt/MCM-41 is retained after depositing Pt on the support. While the TEM images represent the local structure of particular Pt/MCM-41 particles, small angle X-ray diffraction (XRD) gives statistical information for the entire Pt/MCM-41 structure. From the XRD patterns of Pt/MCM-41 (Fig. 3a), four peaks can be identified located at 2.17° (normalized peak intensity 100), 3.80° (16), 4.36° (10), and 5.76° (3), which correspond to the hexagonal mesopore of MCM-41 and are consistent with literature.³⁷ The peak positions and intensity ratios are similar to those of pure MCM-41 (2.14° (100), 3.75° (16), 4.32° (10), and 5.73° (3)), and indicate that the mesoporous architecture is preserved after Pt deposition and high-temperature calcination.

Nitrogen adsorption and desorption experiments indicate that the pores remain largely open and accessible. The isotherm curves of both Pt/MCM-41 and MCM-41 exhibit a typical type IV shape, and are similar to each other (Fig. 3b), as the N_2 adsorption of two sample at each P/P_0 is within 7% difference.

Fig. 3 (a) Small angle XRD pattern and (b) nitrogen adsorption and desorption isotherm of Pt/MCM-41 and MCM-41.

Furthermore, the average pore size of the Pt/MCM-41 was calculated to be 3.1 ± 0.3 nm, which is consistent with the TEM images and, within the experimental error, is the same to that of pure MCM-41 (2.6 ± 0.3 nm). After the deposition of Pt on the zeolite, the surface area of the catalyst was determined to be 612 ± 10 m² g⁻¹, which is slightly lower than the value of 650 ± 5 m² g⁻¹ measured for pure MCM-41. The pore volume decreases from 0.795 ± 0.008 to 0.767 ± 0.017 cm³ g⁻¹. In both cases, less than a 6% reduction is observed after the deposition of Pt.

The catalytic performance of the bi-functional Pt/MCM-41 catalysts towards C_{8+} production was tested in a fix-bed reactor. 2MF and butanal with a molar ratio of 1 : 1 (optimal stoichiometric ratio for C_9 production) are reacted with hydrogen under 3.5 MPa at various temperatures. As shown in the Table 1 at 623 K, 100% conversion of 2MF is achieved over the Pt/MCM-41 catalysts, with a $69 \pm 7\%$ selectivity to C_{8+} hydrocarbons. The yield to C_{8+} (69%) is somewhat lower than that reported previously for the two-step process (87%).²⁰ The lower yield to C_{8+} in our experiments at 623 K could be attributed to the partial cracking of the produced hydrocarbons on the Pt/MCM-41 catalyst, which leads to the formation of shorter hydrocarbons

Table 1 Catalytic performances of bi-functional catalysts for C₈₊ production from 2-methylfuran

Catalysts	Temperature (K)	Conversion ^a (%)	Selectivity to C ₈₊ ^b (diesel) (%)	C ₈₊ yield (%)
0.1 wt%	623	100	69	69
Pt/MCM-41	553	100	76	76
	503	98	98	96

^a Conversion is calculated by dividing moles of converted 2MF to original moles of 2MF measured by GC-MS. The error of calculated conversion is $\pm 4\%$. The butanal has the same conversion as the reactant is added with stoichiometric ratio, and was measured also by GC-MS. ^b The selectivity to C₈₊ is calculated by the portion of carbon from the 2MF and butanal converted to C₈₊ hydrocarbons, and is measured by GC-MS. The error for the calculated selectivity is $\pm 7\%$.

Fig. 4 (a) Influence of temperature on the product distribution over Pt/MCM-41, and (b) detailed product distribution at 503 K over Pt/MCM-41 (the percentage is calculated based on the percentage of carbon in each product). The C₁₄O₂H₈ stands for 1,1-bisylvlbutane in (b).

(mainly C₇), see Fig. 4a. Lowering the reaction temperature from 623 to 553 K increases the C₈₊ selectivity from 69% to 76%, while decreasing the selectivity to C₇. This result is expected since cracking reactions are favored at higher temperatures.^{38,39} Lowering the reaction temperature to 503 K further increases the C₈₊ selectivity to 98%, as shown in Table 1 and Fig. 4. At 503 K, the

overall yield to C₈₊ is 96%, higher than the yield (87%) obtained with the two-step process.²⁰ Upon further lowering the reaction temperature to 463 K, there is significant amount of 1,1-bisylvlbutane produced beside the C₈₊ hydrocarbons. The 1,1-bisylvlbutane is also observed at a reaction temperature of 503 K, suggesting that 2MF and butanal go through the alkylation reaction first and then undergo hydrodeoxygenation to form C₈₊. During the reaction at 463 K, tetrahydrofuran and butanol are also produced, and may arise from side reactions of biofuel production. It is suspected that at 463 K, the rate of the main reaction is much lower than that at 503 K or above, and that side reactions, such as the hydrogenation of 2MF and butanal, become dominant at such low temperatures. These results indicate that the temperature plays an important role in the C₈₊ production by influencing the competition between main and side reactions.

To make the bi-functional catalyst viable for C₈₊ production, the catalyst must not only have high yield, as demonstrated, but must also be stable under reaction conditions. Because thermal treatment (>373 K) may destroy the pore system of MCM-41 by either dealumination or coking,^{40–42} the stability of the Pt/MCM-41 catalysts was tested at 623 K, the highest reaction temperature employed in this study, by keeping the same catalyst batch four times on stream for 20 hours with a reactor shut down between the reaction cycles. As shown in Fig. 5a, the conversion of 2MF and the selectivity to C₈₊ are retained at 100% and 69 $\pm$ 7%, respectively, which indicates excellent thermal stability of Pt/MCM-41 over multiple reaction cycles. As shown in Fig. 5b, the ordered pore structure of MCM-41 can be clearly identified in the TEM image of the used Pt/MCM-41 catalyst. Furthermore, the nitrogen adsorption and desorption isotherms taken on the used catalyst show the typical type IV isotherm curve, as was observed before see Fig. 5c. This result is consistent with literature reports demonstrating that MCM-41 with high Si:Al ratios can retain part of the mesoporous structure after hydrothermal treatment.^{40,41} Thus, the stability tests, TEM images, and nitrogen isotherm curves indicate that Pt/MCM-41 has a good stability for the C₈₊ production (Scheme 2).

For future catalyst development, it is important to understand how C₈₊ hydrocarbons are produced on the bi-functional catalysts. Four possible reaction pathways are proposed for the C₈₊ production on the bi-functional catalyst. The first feasible route is that 2MF and butanal go through an alkylation reaction at beginning to form 1-bisylvl-butanol, followed by hydrodeoxygenation reaction to form C₉H₂₀ (main C₈₊ hydrocarbon product), as shown in route 1 in Scheme 2. Similar to the route 1, in routes 2–4, the 2MF and/or butanal may first go through hydrogenation to 2-methyltetrahydrofuran (2MTHF) and/or 1-butanol, followed by the alkylation reaction and hydrodeoxygenation reaction to form C₉H₂₀. Due to the extra hydrogenation steps needed for routes 2–4, more active sites for hydrogenation/hydrodeoxygenation are expected. Since noble metals, such as platinum, are usually used for the hydrogenation/hydrodeoxygenation, the requirement for more active sites will likely increase the catalyst cost, even though increasing of catalyst disperse can also increase active site number.

To test the feasibility of the reaction pathways, *in situ* DRIFTS has been adopted to follow hydroxyl groups that will

Fig. 5 (a) Time-on-stream data for the Pt/MCM-41 catalyst for C_{8+} production (each run equals 20 hours of time on stream), (b) TEM image, and (c) nitrogen adsorption and desorption isotherm of the after-reaction Pt/MCM-41 catalyst.

be formed during the reaction. A significant difference between the four possible reaction routes is that to form hydroxyl species, hydrogen is required for routes 2–4, while for route 1, the hydroxyl species can be formed through direct the alkylation reaction between 2-MF and butanal without the presence of hydrogen. Thus, we performed *in situ* DRIFT experiments on the Pt/MCM-41 catalysts with 2-MF and butanal carried by He

Scheme 2 Reaction pathways for the C_{8+} production on the Pt/MCM-41.

Fig. 6 *In situ* DRIFT spectrum of Pt/MCM-41 under a mixed gas environment containing 2-methylfuran, butanal, and He at 333 K.

instead of H_2 . The spectra were background corrected using a background obtained under pure He and a representative result is shown in Fig. 6. A broad peak corresponding to the O–H stretching vibration is observed in the spectral range between $3600\text{--}3000\text{ cm}^{-1}$, along with multiple peaks associated with C–H stretching vibrations between $2650\text{--}3000\text{ cm}^{-1}$. The formation of O–H species on the Pt/MCM-41 catalyst indicates that the alkylation between 2-MF and butanal can proceed without the presence of H_2 in the reaction feed. This is consistent with our results from the batch reactions for screening of catalyst support. During the batch reactions, alkylation reaction between 2MF and butanal without H_2 assistance has been observed, as was shown in Fig. 1. Therefore, the DRIFT spectra indicate that pathway 1 is a possible reaction pathway for C_{8+} production on Pt/MCM-41.

Table 2 Influence of gas environment on the conversion of 2-methylfuran on Pt/MCM-41

Reactions	Conversion ^a (%)
2MF + butanal + H ₂ ^b	69 ^c
2MF + butanal + Ar	62

^a Tested under 100 psi, conversion calculated based on the amount of 2MF before and after reaction. ^b Keep all other reaction conditions the same, including the GHSV, pressure, the activation procedure, the amount of catalyst. ^c Measured with FID detector on GC-MS.

Even though the *in situ* DRIFT spectra show that the alkylation reaction in route 1 is feasible, the reaction rate of the alkylation may be too slow to compete with routes 2–4. To be the dominate pathway for C₈₊ production, reaction 1 should be the kinetically preferred route, as compared to its competitors (route 2–4 in Scheme 2). To find the most favorable routes, the reaction rates of route 1–4 are compared with a set of batch reactions between 2MF or 2MTHF and butanal or 1-butanol carried out under atmospheric pressure to test whether routes 2–4 are competitive with route 1. The reaction between 2MF and butanal stands for the route 1, the reaction between 2MTHF and 1-butanol for route 2, 2MTHF and butanal for route 3, and 2MF and 1-butanol for route 4. The reaction conditions are kept the same for each of those batch reactions. All four batch reactions simulate one of the most important steps in routes 1–4, that is the chain growth by hydroalkylation reaction. While the reaction between 2MF and butanal gives 62% conversion of 2MF, the other reactions show no conversion of 2MF or 2MTHF. Thus, this comparison indicates then route 1 is not only feasible but also the kinetically favorable pathway for C₈₊ production on Pt/MCM-41.

To further confirm that route 1 is the dominate pathway for C₈₊ production, two steady-state fixed bed reactions were compared to demonstrate whether the conversion of the 2MF and butanal without hydrogen present is similar to that with hydrogen assistance. The experiment with H₂ represents the reaction for C₈₊ production, while the second condition under Ar represents the reaction for the route 1, as shown in Scheme 2. If the C₈₊ production follows route 1, both reactions under H₂ or Ar should exhibit very similar conversion of 2MF. The two reactions are performed at similar reaction conditions as those that have been used for C₈₊ production. However, the total pressure in the reactor was lowered from 3.4 MPa to 0.7 MPa due to limitation of the pressure reducing valve for Ar. As seen in Table 2, the reaction under Ar shows considerable conversion of 2MF (62%), a value similar to that observed under H₂ (69%). This result agrees with the previous batch reaction tests and confirms that route 1 is indeed the dominate reaction pathway for C₈₊ production.

4 Conclusions

A bi-functional Pt/MCM-41 catalyst has demonstrated an overall reaction yield of 96% for the conversion of waste-biomass derived 2MF and butanal to drop-in fuels. The MCM-41 works

as support for Pt, and also supplies acid sites for the alkylation reaction between 2-methylfuran and butanal to form long chain carbohydrates, which are then hydrodeoxygenated to hydrocarbons on the Pt. The production of C₈₊ on Pt/MCM-41 is sensitive to the reaction temperature, which influences the selectivity to hydrocarbon fuels and chain length of side-products. Based on *in situ* IR spectra and steady-state reaction experiments, a reaction pathway is proposed, consisting of the alkylation reaction of 2MF and butanal followed by hydrodeoxygenation.

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