Supporting information

Synthesis of diesel and jet fuel range alkanes with furfural and ketones from lignocellulose under solvent free conditions

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1. Preparation of catalysts

CaO sample was purchased from Aladdin Reagent Company and calcined under nitrogen atmosphere at 873 K for 4 h.

MgO was prepared by thermal decomposition of MgCO$_3$ in nitrogen flow at 973 K for 4 h.

MgO-ZrO$_2$ mixed oxide was synthesized with magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O) and zirconyl nitrate (ZrO(NO$_3$)$_2$·6H$_2$O) according to the method described in literature.$^1$

KF/Al$_2$O$_3$ was obtained by the wet impregnation of $\gamma$-Al$_2$O$_3$ with an aqueous solution of KF followed by drying at 393 K overnight. The KF loading on catalyst is 40% by weight (denoted as 40 wt.%).

MgAl-hydrotalcite (MgAl-HT, Mg/Al atomic ratio = 3) was prepared according to literature.$^{1-2}$ A solution of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O in 200 mL deionized water was pumped into a mixture of NaOH and Na$_2$CO$_3$. The addition process was conducted at 343 K water bath under vigorous mechanical agitation. Then the gel was aged at this temperature for 16 h. The solid as obtained was filtered, washed until filtrate pH became 7 and dried overnight at 353 K. The dried precursor was calcined in nitrogen flow at 723 K for 8 h.

CoAl-hydrotalcite (CoAl-HT, Co/Al atomic ratio = 1.5) was prepared by conventional co-precipitation method$^3$ from an aqueous solution (100 mL) containing 0.027 mol Co(NO$_3$)$_2$·6H$_2$O and 0.018 mol Al(NO$_3$)$_3$·9H$_2$O and a basic solution (100 mL) containing 0.13 mol NaOH and 0.065 mol Na$_2$CO$_3$. They were added dropwise into 250 mL of deionized water at room temperature under vigorous stirring to maintain the pH around 10. Then the mixture was aged at 353 K for 1 day under magnetic stirring. After filtering and washing to neutral, the resulting CoAl-HT precursor was dried, then calcined at 573 K.

All of the base catalysts were activated in N$_2$ atmosphere for 2 h at their calcination temperature before being used as the catalysts for aldol condensation.
Silica-alumina $\text{SiO}_2-\text{Al}_2\text{O}_3$ ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) support used in hydrodeoxygenation of aldol condensation product was purchased from Qingdao Ocean Chemical Ltd. H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) and H-Î± ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) zeolites were provided by Nankai University.

The Pd catalysts used in HDO reaction were prepared by the incipient wetness impregnation of different supports with the aqueous solution of $\text{PdCl}_2$ in diluted HCl. To facilitate the comparison, the theoretical Pd contents in all catalysts were fixed as 5 wt.%. After being dried at room temperature for 24 h, the catalysts were reduced by $\text{H}_2$ flow (60 mL min$^{-1}$ g$^{-1}$) at 623 K for 2 h, cooled down to room temperature and passivated with 1% $\text{O}_2$ in $\text{N}_2$.

2. Activity test

2.1. Aldol condensation

The aldol condensations of furfural with different ketones were carried out in Parr batch reactor. Typically, 1.92 g (20 mmol) furfural, 60 mmol ketone and 0.36 g catalyst were put into the reactor. Before the reaction, the reactor was purged with Ar. The mixture was stirred at 403 K for 6 h. After being cooled down to room temperature, the liquid product was filtered and analyzed by an Agilent 1100 HPLC equipped with a ZORBAX SB-C18 (4.6×150 mm, 5 mm) column and refractive index detector (RID). The solution of methanol and water (10:1 v/v) was used as the eluent. The furfural conversion was calculated by its consumption. The carbon yield of 1-(2-furanyl)-1-hexen-3-one (i.e. 1a in Scheme 1) or 1-(2-furanyl)-1-Octen-3-one (i.e. 1b in Scheme 1) was defined as: $(\text{The mole of 1a (or 1b) generated during the reaction})/(\text{The mole of furfural in the feedstock}) \times 100\%$. It is interesting that the conversions of furfural observed in this work are always slightly higher than the carbon yields of aldol condensation products (i.e. 1a and 1b in Scheme 1), although no evident peak of by-product was identified by HPLC analysis (see Figure S1). These small differences can be explained by two reasons:
1) The adsorption of furfural on the surfaces of the solid base catalysts. 2) The Cannizzaro reaction of furfural under the catalysis of solid base will produce furoic acid and furfuryl alcohol. The furfuryl alcohol can further react with water (generated from the aldol condensation of furfural and ketones) and produce levulinic acid. Both furoic acid and levulinic acid can react with the solid base catalyst and lead to the decrease of active sites. This may be the reason why we didn’t observed the peak of furoic acid, furfuryl alcohol or levulinic acid in HPLC chromatograms but noticed the evident deactivation of the solid base catalyst after being used in the aldol condensation.

The reusability of CaO catalyst was investigated under the same reaction conditions as we used in the screening of catalysts (403 K, 6 h, 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g catalyst). After each usage, the catalyst was filtrated, thoroughly washed with methanol, dried at 333 K for 8 h and regenerated in air flow at 873 K for 4 h before it was used for another batch reaction.

The 1-(2-furanyl)-1-hexen-3-one and 1-(2-furanyl)-1-octen-3-one which were separated from unreacted furfural, unreacted ketones and by-products by vacuum distillation were kept in refrigerator and used in the following hydrodeoxygenation step.

2.2. Hydrodeoxygenation

The hydrodeoxygenation (HDO) of the aldol condensation product(s) was carried out at 533 K in a 316L stainless steel tubular flow reactor described in our previous work. For each reaction, 1.8 g catalyst was used. The purified aldol condensation product which has high purity (according to HPLC and NMR analysis) and similar component (C: 72.0 wt%; H: 7.7 wt%; O: 18.7 wt%) as theoretical ones (C: 73.1 wt%; H: 7.4 wt%; O: 19.5 wt%) was pumped into the reactor at 0.04 mL min$^{-1}$ from the bottom along with hydrogen at a flow rate of 120 mL min$^{-1}$. After passing through a gas-liquid separator, the products became two phases. The gaseous products flowed
through a back pressure regulator to maintain the pressure in reaction system at 6 MPa and were analyzed online by an Agilent 6890N GC. The CO$_2$ in the gaseous product was analyzed by a thermal conductivity detector (TCD) equipped with an Alltech HAYESEP DB 100/120 packed column (30 feet, 1/8 inch O.D., 2.0 mm I.D.). The alkanes in the gaseous product were separated by an Rt®-Q-BOND capillary column (30 m, 0.32 mm I.D., 10 μm film) and analyzed by a flame ionized detector (FID). The liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 6890N GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm I.D., 0.5 μm film) and FID detector.

Method for the calculation of carbon yields in HDO step:

Carbon yield of C$_1$-C$_4$ light alkanes (%) = Sum of carbon in the C$_1$-C$_4$ alkanes detected from the gas phase products in unit time/Carbon fed into the reactor in unit time $\times$ 100%

Carbon yield of C$_5$-C$_8$ gasoline range alkanes (%) = Sum of carbon in the C$_5$-C$_8$ alkanes detected from the gas phase products in unit time/Carbon fed into the reactor in unit time $\times$ 100% + Sum of carbon in the C$_5$-C$_8$ alkanes detected from liquid phase products/Carbon fed into the reactor $\times$ 100%

Carbon yield of C$_9$-C$_{12}$ diesel and jet fuel range alkanes (%) = Sum of carbon in the C$_9$-C$_{12}$ alkanes detected from the liquid phase product/Carbon fed into the reactor $\times$ 100%

3. Characterization

3.1. N$_2$-adsorption

The BET surface areas of the catalysts were determined by nitrogen adsorption at 77 K using an ASAP 2010 apparatus. Before each measurement, the sample was evacuated at 573 K for 3 h.
3.2. XRD

XRD patterns of different Pd catalysts were recorded with a PANalytical X’Pert-Pro powder X-ray diffractometer, using Cu Kα monochromatized radiation (λ = 0.1541 nm) at a scan speed of 5° min⁻¹. From the results shown in Figure S14, we can only observe the peaks of supports and metallic Pd, which means that the Pd species was reduced to metallic state after pretreatment with H₂ at 623 K. The average sizes of Pd particles on different catalysts were estimated by Debye-Scherrer equation (see Table 3).

3.3. Hydrogen-oxygen titration

The Pd dispersions over different Pd catalysts were determined by the method of hydrogen-oxygen titration using a Micromeritics Autochem II 2920 automated chemisorption analyzer. Prior to measurement, the sample was pretreated at 623 K for 1 h in a flow of 10% H₂/Ar, purged in Ar at 633 K for 30 min and cooled down to 323 K in Ar. Subsequently, the pre-oxidation of sample was performed by switching to a flow of 2% O₂/He for 30 min to form Pd-O surface species, and then purged with argon for 30 min. Finally, 10% H₂/Ar was dosed until all surface Pd-O species reacted with hydrogen to form water and Pd–H surface species. The metal dispersions of different Pd catalysts (see Table 3) were calculated by the hydrogen consumption which was quantitatively measured with a high sensitivity thermal conductivity detector (TCD) (assuming 1.5 H₂ molecules are consumed for each surface Pd atom). From the results listed in Table 3, the metal dispersions of the Pd catalysts are relatively low. This can be explained by the preparation method of Pd catalysts (incipient wetness impregnation). For zeolite catalysts, another reason for the low dispersion of Pd on catalysts is the electrostatic repulsive force between PdCl₄²⁻, PdCl₃(H₂O)⁻ species and zeolite frameworks which are also negative in charge.

3.4. CO₂-TPD

The basicity of the different solid base catalysts used in this work were characterized by the CO₂-TPD which was carried out with a Micromeritics AutoChem
II 2920 Automated Catalyst Characterization System. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at its preparation temperature for 1 h and cooled down in He flow to 353 K. After the saturated adsorption of CO$_2$ by impulse injection, the sample was heated at 353 K in He for 45 min to remove the physically adsorbed CO$_2$. Desorption of CO$_2$ was conducted in He flow from 353 K to 1073 K at a heating rate of 10 K min$^{-1}$. The desorbed CO$_2$ molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit.

3.5. NH$_3$-TPD

The acidities of the different solid base catalysts used in this work were characterized by the NH$_3$-TPD which was carried out with the same system as we used for CO$_2$-TPD. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at 393 K for 1 h and cooled down in He flow to 373 K. After the saturated adsorption NH$_3$, the sample was heated at 373 K in He for 45 min to remove the physically adsorbed NH$_3$. Desorption of NH$_3$ was conducted in He flow from 373 K to 1073 K at a heating rate of 10 K min$^{-1}$. The desorbed NH$_3$ molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit.

3.6. FT-IR of pyridine adsorption

FT-IR spectra with pyridine as probe molecular were collected using a Bruker Equinox 55 FT-IR instrument equipped with a DTGS detector which was operated at a resolution of 2 cm$^{-1}$. For each test, the sample wafer was loaded into a quartz IR cell with CaF$_2$ windows, treated under pure He flow at 473 K for 1 h, evacuated at the same temperature for 30 min and cooled down to room temperature. At this stage, the spectrum was collected as the background reference. The adsorption of pyridine was carried out by exposing the catalyst wafer to pyridine vapour (5 Torr) at room temperature for 30 min. Then the sample was evacuated at the same temperature for 30 min. The spectra were recorded after the desorption of pyridine in vacuum at 373 K for 20 min and cooling to room temperature. By subtracting
the spectrum of the background, the final IR spectrum were obtained. The ratios of Brønsted acid to Lewis acid (B/L ratio) on the surfaces of different supports were calculated by the integral intensities of the individual bands characteristic of pyridine on Brønsted acid sites (at 1540 cm\(^{-1}\)) and Lewis acid sites (at 1450 cm\(^{-1}\)) in combination with the molar absorption coefficients of \(e(B) = 1.67 \text{ cm umol}^{-1}\) and \(e(L) = 2.22 \text{ cm umol}^{-1}\). The amounts of Brønsted acid sites were calculated by the B/L ratios and the total amounts of acid sites over different catalysts.
Figure S1. HPLC chromatograms of the liquid products from the aldol condensation of furfural with 2-pentanone (a) or 2-heptanone (b).
Figure S2. $^{13}$C and $^1$H NMR spectra of 1a from the aldol condensation of furfural with 2-pentanone.
Figure S3. HPLC chromatograms of the liquid products from the self aldol condensation of 2-pentanone (a) or 2-heptanone (b). Reaction conditions: 60 mmol 2-pentanone (or 2-heptanone) and 0.36 g CaO catalyst at 403 K for 6 h.
**Figure S4.** Conversions of furfural and the yields of 1-(2-furanyl)-1-hexen-3-one (1a) over the CaO catalyst as the function of reaction time. Reaction conditions: 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g catalyst at 403 K in a batch reactor.
Figure S5. Conversions of furfural (solid symbols) and carbon yields of 1a (empty symbols) over fresh (■, □), the first regenerated (▲, △) and the second regenerated (●, ○) CaO catalysts. Reaction conditions: 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g catalyst at 403 K in a batch reactor.
Figure S6. Concentrations of furfural (empty symbols) and 1a (solid symbols) in the reaction mixture as the function of reaction time. Reaction conditions: 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g fresh (□,■), the first regenerated (△,▲), and the second regenerated (○,●) CaO catalysts catalyst at 403 K in a batch reactor.
Figure S7. $^{13}\text{C}$ and $^1\text{H}$ NMR spectra of $\text{1b}$ from the aldol condensation of furfural with 2-heptanone.
Figure S8. Carbon yields of C$_1$-C$_4$ light alkanes (black bar), C$_5$-C$_8$ gasoline range alkanes (white bar), C$_9$-C$_{10}$ diesel and jet fuel range alkanes (grey bar) over Pd/H-ZSM-5 and Pd/H-β catalysts. Reaction conditions: 533 K, 6 MPa, 1.8 g catalyst; liquid feedstock 1-(2-furanyl)-1-hexen-3-one (i.e. 1a in Scheme 1) flow rate: 0.08 mL min$^{-1}$; hydrogen flow rate: 120 mL min$^{-1}$. 
Figure S9. Carbon yields of C$_1$-C$_4$ light alkanes (black bar), C$_5$-C$_8$ gasoline range alkanes (white bar), C$_9$-C$_{10}$ diesel and jet fuel range alkanes (grey bar) over Pd/H-ZSM-5 as the function of 1-(2-furanyl)-1-hexen-3-one (i.e. 1a in Scheme 1) flow rate. Reaction conditions: 533 K, 6 MPa; 1.8 g catalyst; hydrogen flow rate: 120 mL min$^{-1}$. 

![Graph showing carbon yield vs. flow rate of 1a](image-url)
Figure S10. Chromatograms of liquid samples from the HDO of 1-(2-furanyl)-1-hexen-3-one (i.e. 1a in Scheme 1) over Pd/H-ZSM-5. Reaction conditions: 533 K, 1.8 g catalyst; hydrogen flow rate: 120 mL min$^{-1}$, liquid feedstock 1a flowrate: (a) 0.08 mL min$^{-1}$, (b) 0.12 mL min$^{-1}$.
**Figure S11.** Some possible reaction pathways for the production of C₉-C₁₂ alkanes by the HDO of 1a and 1b.
Figure S12. Conversions of furfural (●), yields of 1a (▲) and 1b (▼) over CaO catalyst. Reaction conditions: 20 mmol furfural, 40 mmol 2-pentanone, 20 mmol 2-heptanone and 0.36 g CaO catalyst, 6 h in a batch reactor.
**Figure S13.** Conversions of furfural (white bar), yields of 1a (black bar) and 1b (grey bar) over different solid base catalysts. Reaction conditions: 20 mmol furfural, 40 mmol 2-pentanone, 20 mmol 2-heptanone and 0.36 g catalyst, at 403 K for 6 h in a batch reactor.
Figure S14. XRD patterns of different Pd catalysts
Figure S15. FT-IR spectra of different supports after adsorption of pyridine and vacuation at 373 K. B: Brønsted acid sites, L: Lewis acid sites.
References


