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

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C₉-C₁₂ alkanes were first synthesized at high overall yield (~80%) with the furfural, 2-pentanone, and 2-heptanone from lignocellulose.

COMMUNICATION

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

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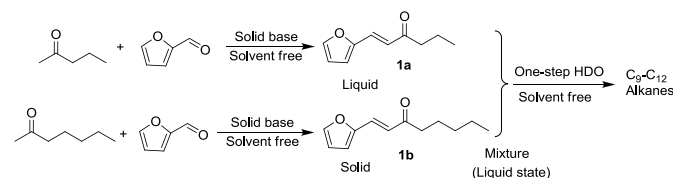
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Under solvent-free conditions, C₉-C₁₂ alkanes were first synthesized at high overall carbon yield (~80%) by the solid base catalyzed aldol condensation of furfural with 2-pentanone (or a mixture of 2-pentanone and 2-heptanone) from lignocellulose, followed by direct hydrodeoxygenation over Pd loaded solid acid catalysts at 533 K.

As a result of the declining fossil energy and the increasing environmental problems, the catalytic conversion of biomass and derivatives into fuels¹ and value-added chemicals² has gained tremendous attention. Diesel and jet fuel are two kinds of often used transportation fuels which are mainly obtained from petroleum nowadays. Lignocellulose is the major component of agriculture wastes and forest residues. Pioneered by the works of Dumesic group³ and Huber *et al.*,³⁻⁴ the synthesis of diesel and jet fuel range alkanes with the lignocellulose derived platform chemicals is attracting more and more interests.⁵ Furfural is an important chemical which has been produced on industrial scale by the hydrolysis-dehydration of the hemicellulose.⁶ In the recent works of Dumesic^{3a,7} and Huber *et al.*,⁴ C₈ and C₁₃ oxygenates were produced by the aldol condensation of furfural and acetone. These oxygenates can be converted to C₈-C₁₃ alkanes by low temperature hydrogenation and hydrodeoxygenation (HDO). Because the aldol condensation products of furfural and acetone are solid, organic solvent is necessary for the aldol condensation and subsequent hydrogenation step to obtain better mass transfer. This will lead to higher cost and lower efficiency of energy and facility. To fulfill the need of real application, new routes for the solvent-free synthesis of diesel and jet fuel range alkanes should be developed.

2-Pentanone is a by-product in the selective hydrogenation of furfural to 2-methylfuran, a feedstock in the production of diesel and jet fuel range branched alkanes.⁸ In the recent works of Anbarasan *et al.*^{5a} and Mou group⁹, 2-pentanone and 2-heptanone were obtained simultaneously by the Pd/C and K₃PO₄ catalyzed alkylation of the acetone-*n*-butanol-ethanol (ABE) fermentation products from lignocellulose. In this work, we reported, for the first time, the solvent-free synthesis of diesel and jet fuel range alkanes by the aldol condensation of furfural with 2-pentanone (or the mixture of 2-pentanone and 2-heptanone), followed by the one-step HDO process (Scheme 1). By taking advantage of the good intersolubility of solid

aldol condensation product **1b** in liquid aldol condensation product **1a**, we successfully prepared C₉-C₁₂ straight alkanes without using of any solvent during the whole process.



Scheme 1. Synthetic route of diesel and jet fuel range alkanes using furfural and ketones from lignocellulose.

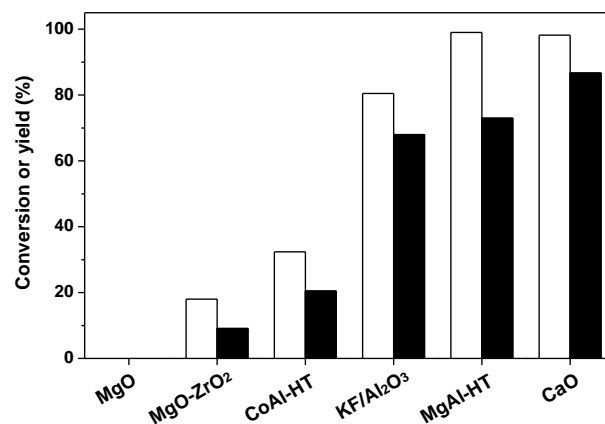


Figure 1. Conversions of furfural (white bar) and carbon yields of **1a** (black bar) over different solid bases. Reaction conditions: 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g catalyst at 403 K for 6 h.

A series of solid bases were investigated for the solvent-free aldol condensation of furfural and 2-pentanone. From the analysis of HPLC and NMR (see Figure S1 and S2 in supporting information), 1-(2-furanyl)-1-hexen-3-one (*i.e.* **1a** in Scheme 1) was identified as the main product. In contrast, the self aldol condensation product of 2-pentanone was not identified in the liquid product, indicating that 2-pentanone only reacts with furfural under the investigated conditions. The impossibility for the self aldol condensation of 2-pentanone under the investigated conditions was further confirmed

by the blank experiment with 2-pentanone as the only reactant (the HPLC chromatogram of liquid product was shown in Figure S3). After purification, the **1a** as obtained is liquid at room temperature.¹⁰ Therefore, it can be directly used for the HDO process. In real application, this is advantageous because the hydrogenation and hydrodeoxygenation steps can be combined into one-step, which will decrease the facility investment and energy consumption.

Figure 1 shows the conversions of furfural and the yields of **1a** over different solid bases. Among them, the CaO exhibited the best catalytic performance (98.3% conversion, 86.7% yield) for the aldol condensation of furfural and 2-pentanone. The activity sequence of different catalysts is CaO > MgAl-hydrotalcite (MgAl-HT) > KF/Al₂O₃ > CoAl-hydrotalcite (CoAl-HT) > MgO-ZrO₂ > MgO. To check the homogeneous contribution of the Ca species which was dissolved in the reaction mixture, we also investigated the effect of reaction time on the furfural conversion and the 1-(2-furanyl)-1-hexen-3-one (*i.e.* **1a**) yield over CaO catalyst. From the results illustrated in Figure S4, 53% furfural conversion and 34% **1a** yield were achieved after reacting at 403 K for 0.5 h. Using the reaction mixture filtered at this time, we ran another batch of reaction immediately. No change of furfural conversion or **1a** yield was noticed after reacting at 403 K for another 4 h. According to this result, we believed that the homogeneous contribution of the Ca species dissolved in reaction mixture is negligible.

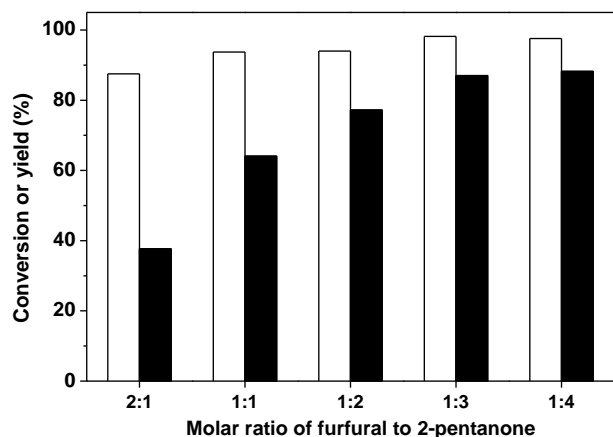


Figure 2. Conversions of furfural (white bar) and carbon yields of **1a** (black bar) over CaO as the function of initial molar ratio of furfural to 2-pentanone. Reaction conditions: 1.92 g (20 mmol) furfural and 0.36 g catalyst at 403 K for 6 h.

The effect of furfural to 2-pentanone molar ratio on the yield of **1a** over CaO was investigated. According to Figure 2, the best result was achieved at the initial furfural/2-pentanone molar ratio of 1:3. That is the reason why we chose this ratio to screen the solid base catalysts. It is very interesting that high **1a** yield (65%) can also be obtained over CaO when the initial furfural/2-pentanone molar ratio is 1:1. This result further confirmed that the aldol condensation of furfural and 2-pentanone can be carried out under solvent-free conditions. The reusability of CaO catalyst was checked. Similar to what has been observed by Dumesic group in their previous work about the aldol condensation of furfural and acetone¹¹, evident deactivation of CaO catalyst was observed after it being used in the aldol condensation of furfural and 2-pentanone. However, the activity of CaO catalyst can be almost recovered to its initial level by the regeneration in air flow at 873 K for 4 h. From Figure 3, no evident decrease of furfural conversion or the yield of **1a** was observed over CaO catalyst even after it being used in the aldol condensation and regenerated in air flow for 4 times. Moreover, we also compared the conversions of furfural and the yields of **1a** over the fresh or the regenerated CaO catalysts as the function of reaction

time. According to the results shown in the Figure S5 and Figure S6, slight decreases in the furfural conversion and **1a** yield were observed over the regenerated catalysts in the first 2 h. With the further increasing of the reaction time, the difference between the fresh and the regenerated CaO catalysts becomes less and less evident. The slight deactivation of CaO catalyst might be explained by the carbon deposition or the loss of active sites by the structure change during the aldol condensation and/or the regeneration steps. However, such a slight deactivation doesn't influence the final yield of **1a** over CaO catalyst.

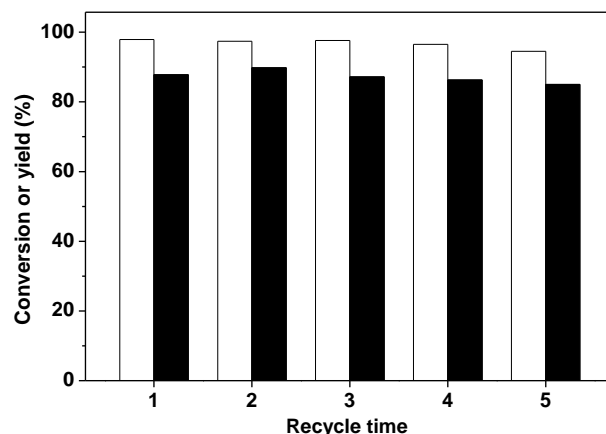


Figure 3. Conversions of furfural (white bar) and carbon yields of **1a** (black bar) over CaO as the function of recycle time. Reaction conditions: 1.92 g (20 mmol) furfural, 5.16 g (60 mmol) 2-pentanone and 0.36 g catalyst at 403 K for 6 h.

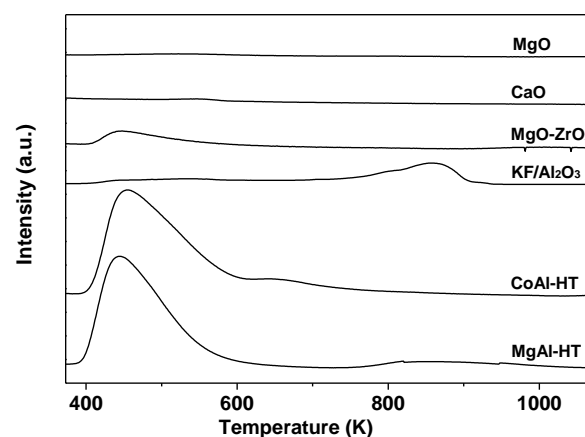


Figure 4. NH₃-TPD profiles of different solid base catalysts.

Aldol condensation is a reaction which can be catalyzed by either acid sites¹² or base sites¹³. In some works,¹⁴ it was also suggested the synergism effect of acid sites and base sites is beneficial in some reaction systems. In order to find out the reason for the excellent performance of CaO catalyst in the aldol condensation of furfural and 2-pentanone, we characterized the specific surface areas, acidities and basicity of different catalysts by N₂ physical adsorption, NH₃-TPD and CO₂-TPD, respectively. From the results in Table 1, and Figure 4, no evident relationship between the specific BET surface areas or acidities (including the amount or strength of acid sites) of the catalysts and their activities in the aldol condensation of furfural and 2-pentanone was observed. Analogously, the relationship between the activity and the amount of base site over different solid base catalysts is also ambiguous. However, there is distinct correspondence between the activities of the catalysts and

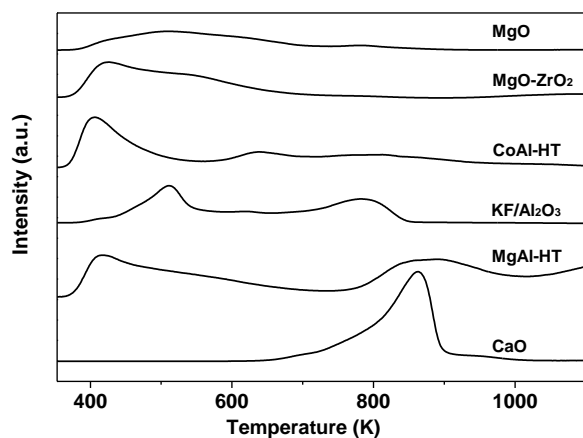


Figure 5. CO₂-TPD profiles of different solid base catalysts.

their base strength which is indicated by the desorption temperature of CO₂ from the catalyst surfaces (see Figure 5). Take MgO and CaO for example, these catalysts have similar chemical structures (because the Mg and Ca are in the same group in periodic table of the elements). However, their catalytic behavior is totally different: MgO is inactive for the aldol condensation of furfural and 2-pentanone, while CaO exhibits excellent performance for the same reaction. From the CO₂-TPD results shown in Figure 5, only a broad peak from 363 K to 723 K was observed in the CO₂-TPD profile of MgO. In contrast, evident CO₂ desorption peak centered at higher temperature (863 K) was observed in the CO₂-TPD profile of CaO. It can be seen that CaO catalyst has higher base strength than that of MgO, which may be the reason for their activity difference. Based on these results, we believe that 1) the reaction mechanism and the role of acid/basic sites in the aldol condensation are also depended on the reaction media. 2) The strong base sites are the active centers for the aldol condensation of furfural with 2-pentanone under solvent-free conditions.

Table 1. Specific BET surface areas, the amounts of base sites and acid sites on different solid base catalysts.

Catalyst	S _{BET} (m ² g ⁻¹)	Base site amount (mmol g ⁻¹)	Acid site amount (mmol g ⁻¹)
MgO	56	0.09	0.02
MgO-ZrO ₂	126	0.16	0.08
KF/Al ₂ O ₃	215	0.08	0.05
CoAl-HT	238	0.13	0.45
MgAl-HT	232	0.21	0.38
CaO	18	0.14	0.03

The aldol condensation of furfural with 2-heptanone was conducted over CaO under the similar reaction conditions (Table 2, entry 2). From the analysis of HPLC and NMR (see Figure S1 and Figure S7), 1-(2-Furanyl)-1-octen-3-one (*i.e.* **1b** in Scheme 1) was gained as the major product with 75.3% yield. Analogous to what we observed in the aldol condensation of furfural and 2-pentanone, there is no self aldol condensation product of 2-heptanone identified in the liquid product. This result indicates that 2-heptanone only reacts with furfural under the investigated conditions. This conclusion was also verified by the blank experiment of 2-heptanone self aldol condensation (see Figure S3 in supporting information). However, **1b** is a yellow solid at room temperature,¹⁰ which can't be directly transported by HPLC pump. In order to solve this problem, we explored the possibility to dissolve the **1b** with **1a** on the basis of the theory of similarity and intermiscibility. As we expected, a liquid

mixture of **1a** and **1b** (after removing catalyst and excess reactants) can be obtained by the simultaneous aldol condensation of furfural with 2-pentanone and 2-heptanone, even at the molar ratio of 2-pentanone to 2-heptanone of 1:2 (Table 2, entry 3). In practical application, the one-pot aldol condensation of furfural-pentanone-heptanone route is advantageous: 1) The cost and energy consumption for the separation of 2-pentanone and 2-heptanone from the direct alkylation of ABE fermentation products can be saved; 2) Higher yield of aldol condensation products can be achieved under the same conditions. According to Table 2, the best carbon yield of aldol products (**1a** and **1b**) was obtained with the 2-pentanone to 2-heptanone molar ratio of 2:1; 3) By this way, the one-step HDO of **1b** can be carried out without using organic solvent, which will also improve the efficiency of energy and facility.

Table 2. Conversion of furfural, yield of **1a** and **1b** over CaO catalyst. Reaction conditions: 403 K, 6 h; 1.92 g (20 mmol) furfural, 60 mmol ketone, 0.36 g catalyst.

Entry	Substrate molar ratio ^a	Conversion of furfural (%)	Yield (%)			Product state ^b
			1a	1b	Total	
1	1:3:0	98.3	86.7	—	86.7	Liquid
2	1:0:3	94.8	—	75.3	75.3	Solid
3	1:1:2	97.8	30.6	56.6	87.2	Liquid
4	1:2:1	97.8	62.0	30.0	92.0	Liquid

a: Molar ratio of furfural: 2-pentanone: 2-heptanone.

b: At room temperature.

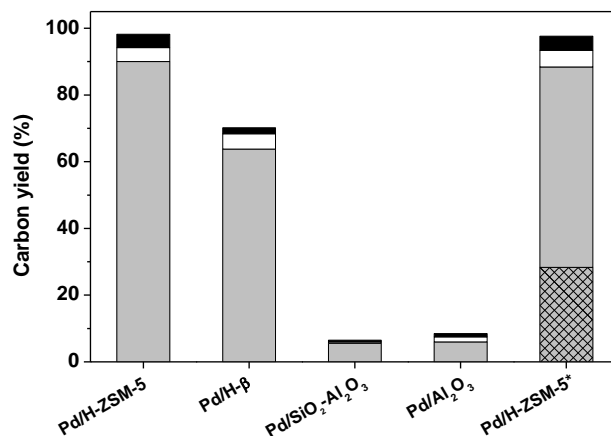


Figure 6. Carbon yields of C₁-C₄ light alkanes (black bar), C₅-C₈ gasoline range alkanes (white bar), C₉-C₁₀ diesel and jet fuel range alkanes (grey bar), C₁₁-C₁₂ diesel and jet fuel range alkanes (grey sparse bar) over different catalysts. Reaction conditions: 533 K, 6 MPa, 1.8 g catalyst; liquid feedstock **1a** (or the mixture of **1a** and **1b** indicated by “**”) flow rate: 0.04 mL min⁻¹; hydrogen flow rate: 120 mL min⁻¹.

As the final aim of this work, we also checked the possibility to make diesel and jet fuel range alkanes by the solvent-free HDO of aldol condensation products. In the previous works of Dumesic group¹⁵ and Ordóñez *et al.*¹⁶, it was found that Pt and Pd catalysts have high activities for the HDO of biomass derived oxygenates. Because the current price of Pd is lower than that of Pt, the utilization of Pd-based HDO catalyst is more economic in real application. Recently, we compared the performances of different metal catalysts for the solvent-free HDO of 5,5'-(butane-1,1-diyl)bis(2-methyl-furan (*i.e.* the hydroalkylation/alkylation product of 2-methylfuran and butanal)¹⁷. Among the investigated candidates, Pd catalysts exhibited excellent HDO activity and the highest selectivity to diesel or jet fuel range alkanes. Due to the above

reasons, we conducted HDO experiments over Pd catalysts supported on solid acids. From Figure 6, evident support effect was observed. Over the Pd/Al₂O₃ and Pd/SiO₂-Al₂O₃ catalysts, low carbon yields (6% and 5.6%, respectively) to diesel and jet fuel range alkanes were achieved. These values were evidently lower than those obtained over Pd/H-β and Pd/H-ZSM-5 catalysts. Among the investigated catalysts, the Pd/H-ZSM-5 exhibited the best performance. Over it, higher carbon yield of diesel and jet fuel range alkanes (90%) can be achieved than those obtained over other Pd catalysts. From the result shown in Figure S8, the activity advantage of Pd/H-ZSM-5 over Pd/H-β is more evident at higher space velocity. This result further proves that Pd/H-ZSM-5 is more active than Pd/H-β in the HDO of **1a**. The stability of Pd/H-ZSM-5 was also checked. During the 24-h continuous test, no evident activity (or selectivity) change was noticed over Pd/H-ZSM-5 (see Figure 7), indicating this catalyst is stable under the investigated conditions. Analogously, up to 88.3% carbon yield of diesel and jet fuel range alkanes was also obtained over Pd/H-ZSM-5 when the mixture of **1a** and **1b** (obtained at the initial furfural: 2-pentanone: 2-heptanone molar ratio of 1:2:1) was used as feedstock.

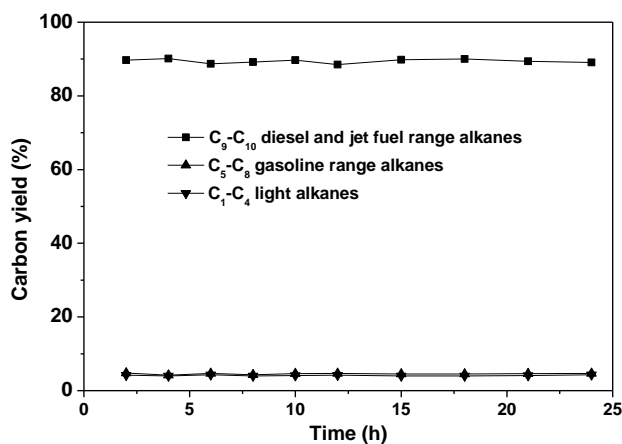


Figure 7. The carbon yields of different alkanes over Pd/H-ZSM-5 as the function of reaction time. Reaction conditions: 533 K, 6 MPa; 1.8 g catalyst; liquid feedstock 1-(2-furanyl)-1-hexen-3-one (*i.e.* **1a** in Scheme 1) flow rate: 0.04 mL min⁻¹; hydrogen flow rate: 120 mL min⁻¹.

We also investigated the effect of space velocity on the catalytic performance of Pd/H-ZSM-5 for the HDO of **1a**. From the results shown in Figure S9 in supporting information, we can see that the carbon yield of alkanes over the Pd/H-ZSM-5 catalyst decreases with the increasing of the **1a** flow rate. At the same time, we also noticed the appearance of oxygenates in the HDO products at **1a** flow rate higher than 0.04 mL min⁻¹ (according to the chromatograms shown in Figure S10). With the increasing of **1a** flow rate, the oxygenates (including 2-hexyltetrahydrofuran and small amount of 1-decanol) becomes the major HDO products. According to the analysis of liquid products from the HDO of **1a** over Pd/H-ZSM-5 catalyst and the reported mechanisms of similar reaction systems,^{5b, 16, 18} the reaction pathways for the production of C₉-C₁₂ alkanes from the HDO of **1a** and **1b** were proposed in Figure S11 in supporting information. At the beginning of the reaction, the C=C bonds, C=O bonds and furan rings in **1a** and **1b** are saturated by hydrogenation. Then the hydrogenated products are further hydrodeoxygenated to decane and dodecane. At the same time, the decarbonylation of the aldehydes generated by furan ring-opening reactions (such as the **2a**, **3a**, **2b** and **3b** in Figure S11) or the dehydrogenation of polyol intermediates (**4a** and **4b** in Figure S11) may lead to the generation of C₉ and C₁₁ oxygenates, which can be further hydrodeoxygenated to nonane and undecane. As another

possibility, nonane and undecane can also be produced by the dehydrogenation of 1-decanol and 1-dodecanol, followed by the decarbonylation of aldehydes as generated (*i.e.* **5a** and **5b** in Figure S11) over Pd particles.

Table 3. Average sizes of Pd particles and metal dispersions on different Pd catalysts.

Catalyst	Average size of Pd particles (nm) ^a	Pd dispersion (%) ^b
Pd/H-ZSM-5	32	2.1
Pd/H-β	25	2.0
Pd/SiO ₂ -Al ₂ O ₃	17	2.5
Pd/Al ₂ O ₃	8	6.4

a: Estimated from XRD results by Debye-Scherrer equation.

b: Measured by hydrogen-oxygen titration.

Table 4. Amounts of acid sites on the surfaces of different supports.

Support	Total amount of acid sites (mmol g ⁻¹)	Brønsted acid to Lewis acid ratio ^a	Amount of Brønsted acid sites (mmol g ⁻¹)
H-ZSM-5	2.00	2.59	1.44
H-β	1.46	1.3	0.83
SiO ₂ -Al ₂ O ₃	0.49	0.02	0.01
Al ₂ O ₃	0.17	0	0

a: Measured by FT-IR with pyridine as probe molecular.

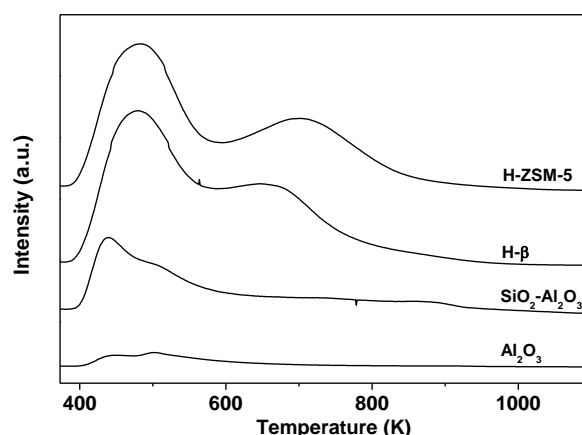


Figure 8. NH₃-TPD profiles of the different solid acid supports.

To figure out the reason for the different performances of Pd catalysts, we characterized them by several technologies. According to the NH₃-TPD and FT-IR results illustrated in Figure 8 and Table 4, H-ZSM-5 has higher acid strength and larger amount of Brønsted acid than those over Al₂O₃, SiO₂-Al₂O₃ and H-β. This may be one reason for the higher HDO activity of Pd/H-ZSM-5 catalyst. As we know, Brønsted acid site is very important in the HDO process. 1) Strong Brønsted acid is more active than weak Brønsted acid for the dehydration which has been considered as an important unit reaction during the HDO of biomass derived oxygenates.¹⁹ 2) Strong Brønsted acid is more active than weak Brønsted acid for the furan ring opening reaction which can greatly decrease the HDO temperature of furan compounds.^{5b, 18b} Besides the acidity of supports, the average sizes of Pd particles on different Pd catalysts can be another possible reason for their activity difference in the HDO of **1a**. From Table 3, the sequence for the average sizes of Pd particles over different Pd catalysts is Pd/H-ZSM-5 > Pd/H-β > Pd/SiO₂-Al₂O₃ > Pd/Al₂O₃. This sequence is basically consistent with the HDO activity sequence of these catalysts. In the previous work of Lercher group²⁰, it has been suggested that larger metal particles are favorable for the HDO of biomass derived oxygenates.

Analogously, we think the larger average Pd particle size on the Pd/H-ZSM-5 catalyst may be another reason for its better catalytic performance in the HDO of aldol condensation product.

Conclusions

In summary, we have demonstrated the first solvent-free synthesis of diesel and jet fuel range alkanes with furfural, 2-pentanone and 2-heptanone which can be obtained from lignocellulose. By the aldol condensation of furfural with 2-pentanone (or the mixture of 2-pentanone and 2-heptanone) over solid base catalysts, followed by the one-step hydrodeoxygenation (HDO) process over Pd catalysts, C₉-C₁₂ alkanes were obtained at high overall carbon yield (~80%). Among the solid base catalysts which were used for the aldol condensation, CaO exhibited the highest activity, which can be rationalized by the stronger basicity of this material. The products from the aldol condensation of furfural and 2-pentanone (or a mixture of 2-pentanone and 2-heptanone) are liquid at room temperature. Therefore, they can be directly hydrodeoxygenated to alkanes over a series of Pd catalysts. Among them, Pd/H-ZSM-5 demonstrated the best catalytic performance and good stability, which makes it a promising catalyst in future application.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental section, catalyst characterization, HPLC chromatograms of liquid products from aldol condensation, NMR spectra of precursors, the activities of regenerated CaO catalysts, the carbon yield of alkanes and the GC chromatograms of the HDO product at higher space velocity]. See DOI: 10.1039/c000000x/

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