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Short Communication

Solvent-free synthesis of C_9 and C_{10} branched alkanes with furfural and 3-pentanone from lignocellulose

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ABSTRACT

Jet fuel range branched alkanes were first synthesized under solvent-free conditions by the aldol condensation of furfural and 3-pentanone from lignocellulose followed by the one-step hydrodeoxygenation (HDO). Among the investigated solid base catalysts, CaO and KF/Al_2O_3 demonstrated the highest activity for the aldol condensation reaction of furfural and 3-pentanone. The aldol condensation product of furfural and 3-pentanone (liquid at room temperature) was directly hydrodeoxygenated to 4-methyl-nonane and 4-methyl-octane. These alkanes have low freezing points (174.1 K and 159.8 K) and can be blended into jet fuel without hydroisomerization. Among the investigated HDO catalysts, the $Ni-Cu/SiO_2$ exhibited the best performance.

1. Introduction

As a solution to the current energy and environmental problems, the catalytic conversion of renewable biomass to fuels and chemicals has drawn tremendous attention [1–3]. Jet fuel is one of the often used liquid fuels, which are mainly produced from petroleum nowadays. Lignocellulose is the main component of agriculture waste and forest residues. In recent years, the synthesis of jet fuel range alkanes with the lignocellulose-derived platform chemicals becomes an active research area [4–7].

Furfural is an important chemical which has been produced in large scale by the catalytic hydrolysis-dehydration of hemicellulose [8]. In the recent works of Dumesic and Huber [4,9–11], it was found that C_8 and C_{13} oxygenates can be obtained by the aldol condensation of furfural and acetone. After the low-temperature hydrogenation and HDO of these oxygenates, C_8-C_{13} alkanes can be obtained (see Scheme 1a). Pioneered by their works, a lot of research was also carried out by other groups about the same reaction system [12,13]. These works open a new era in the production of lignocellulosic biofuel. However, there are also two limitations for the furfural–acetone route: (1) the aldol condensation products of furfural and acetone are solid at room temperature. Therefore, organic solvents were indispensable to facilitate the mass transfer, which will increase the cost and energy consumption. (2) Straight alkanes with lower octane numbers and higher freezing points are produced from the HDO step. Both characters are unfavorable for aviation fuel.

3-Pentanone is the ketonization product of propanoic acid that can be obtained from the dehydration/hydrogenation of lactic acid [14], an important lignocellulosic platform compound [15]. To our knowledge, there is no report about the synthesis of diesel or jet fuel range alkanes with 3-pentanone. In this work, we reported, for the first time, the highly efficient synthesis of C_9 and C_{10} branched alkanes by the aldol condensation of 3-pentanone and furfural followed by the one-step HDO process under solvent-free conditions (Scheme 1b). These branched alkanes have low freezing points and can be blended into jet fuel without hydroisomerization.

2. Experimental

2.1. Catalyst preparation

2.1.1. Solid base catalysts

MgO and CaO were purchased from Kermel Reagent Company. Before being used in reaction, these samples were calcined in nitrogen flow at 873 K for 4 h.

$MgO-ZrO_2$ and $MgO-La_2O_3$ mixed oxide, MgAl hydrotalcite (MgAl-HT) and LiAl hydrotalcite (LiAl-HT) were prepared by the methods introduced in our previous works [16,17].

KF/Al_2O_3 was prepared according to literature [18] by the impregnation of 5.8 g γ-Al_2O_3 with a solution of KF (5 g $KF \cdot 2H_2O$ in 16 g water).

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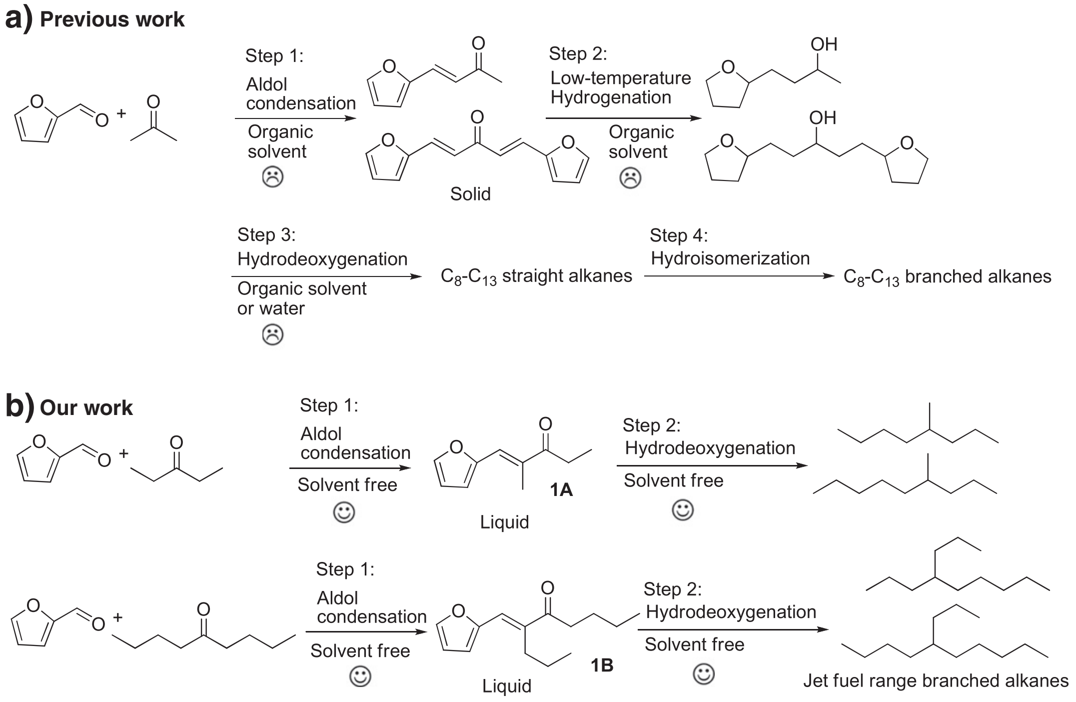

Scheme 1. (a) Previous route versus (b) our new protocol for the synthesis of jet fuel range branched alkanes.

The mixture was stirred at 343 K for 1 h, dried at 393 K for 4 h and calcined in N_2 flow at 873 K for 4 h.

2.1.2. Hydrodeoxygenation (HDO) catalysts

The mono-metallic M/SiO_2 (M = Fe, Co, Ni, Cu, Pt) catalysts were prepared by the incipient wetness impregnation of SiO_2 (Qingdao Ocean Chemical Ltd.) with the aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_3 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $H_2PtCl_6.6H_2O$, respectively. For all these catalysts, the theoretical contents of metal in the M/SiO_2 catalysts were fixed as 5 wt.%. After impregnation, the samples were kept at room temperature for 4 h, dried at 333 K overnight and calcined in air at 773 K for 4 h.

The bimetallic $Ni\text{-}Cu/SiO_2$ catalysts were prepared by the co-impregnation of SiO_2 with the solution of $Ni(NO_3)_3 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$. The total theoretical metal contents of Ni and Cu in the catalysts were controlled as 5 wt.%. To facilitate the comprehension, the weight percentages of Ni and Cu were indicated in the names of $Ni\text{-}Cu/SiO_2$ catalysts. For example, the $Ni4Cu1/SiO_2$ catalyst denotes the $Ni\text{-}Cu/SiO_2$ catalyst containing 4 wt.% Ni and 1 wt.% Cu.

2.2. Activity test

The aldol condensation of furfural and 3-pentanone was performed in batch reactor. Typically, 2.60 g furfural, 4.67 g 3-pentanone and 0.4 g solid base catalyst were used for each test. Before the reaction, the reactor was purged with argon. The mixture was stirred at 443 K for 8 h then cooled down to room temperature. The liquid products were diluted, filtered and analyzed by an Agilent 1260 HPLC equipped with a refractive index detector.

The HDO reaction was carried out in a 316 L stainless steel tubular reactor described in our previous works [16,17]. Prior to reaction, the catalysts (1.8 g) were reduced *in situ* by H_2 flow at 773 K for 2 h. After cooling down the reactor to 623 K and increasing the system pressure to 6 MPa, the aldol condensation product purified by vacuum distillation was pumped into the reactor at 0.04 mL min^{-1} with hydrogen at a flow rate of 120 mL min^{-1}. The products from the outlet of the reactor become two phases in a gas-liquid separator. The gaseous products passed through the back-pressure regulator and were analyzed online by an Agilent 7890A GC. The liquid products were withdrawn periodically from the gas-liquid separator and analyzed by another Agilent 7890A GC.

3. Results and discussion

3.1. Aldol condensation

The solvent-free aldol condensation of furfural and 3-pentanone was carried out over a series of solid bases. From the analysis of HPLC and NMR (see Figs. S1 and S2 in supporting information), 1-(furan-2-yl)-2-methylpent-1-en-3-one (i.e., **1A** in Scheme 1) was identified as the main product. No 1,5-di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one (generated by the aldol condensation of one 3-pentanone molecule with two furfural molecules) was detected in the product even at lower ketone-to-furfural ratio of 0.5. This phenomenon was different with what has been observed in the aldol condensation of furfural with acetone [4,9] and can be explained by the lower reactivity of α-carbon atoms in a 3-pentanone molecule (caused by the electron and steric effects of the methyl groups which are connected with the two α-carbon atoms).

Among the solid base catalysts investigated in this work, CaO and KF/Al_2O_3 exhibited the highest activity for the aldol condensation of furfural and 3-pentanone (see Fig. 1). Over them, about 60% **1A** yields were achieved after reacting at 443 K for 8 h. As we know, CaO is the main component of quick lime. Compared with KF/Al_2O_3, CaO has lower price, wider availability and lower toxicity. Therefore, we believe that CaO is a promising catalyst in future application. Under the same reaction conditions, **1A** yield up to 40% could also be obtained over CaO catalyst at the initial 3-pentanone/furfural molar ratio of 1:1. This result further proved that the reaction can be conducted under solvent-free conditions.

The **1A** as obtained exists as liquid at room temperature, which makes it possible to be directly used in HDO process. In practical application, this is very advantageous because (1) the use of organic solvent can be avoided, which will reduce the cost and energy consumption