Application of Raney Ni and Pt/SiO2-ZrO2 catalysts for two-step hydrogenation of difurfurylidene acetone to long-chain alkanes
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Abstract
Difurfurylidene acetone (F2A) was catalytic converted to long-chain hydrocarbons by a two-step hydrogenation process, low-temperature hydrogenation over Raney Ni catalyst in a batch reactor, followed by hydrodeoxygenation (HDO) over 1wt.%Pt/SiO2-ZrO2 in a fixed-bed reactor. The results indicated that using methanol as solvent promoted hydrogenation of double bonds of F2A over Raney Ni due to its protonation effect. Selectivity of 1,5-di(tetrahydro-2-furanyl)-3-pentanol (II-c), the saturated alcohol form of the hydrogenated dimer, was 72.1% in the hydrogenated intermediate liquid (H-F2A). High carbon alkane yield of liquid alkanes (C8-C14) was 82.9% (mol) after the second-step HDO reaction over 1wt.%Pt/SiO2-ZrO2. Long operation showed the stability of 1wt.%Pt/SiO2-ZrO2 as HDO catalyst, deduced from the steady phase structures of the SiO2-ZrO2 support and Pt active centers during HDO reaction.

Keywords: Raney Ni; 1wt.%Pt/SiO2-ZrO2; difurfurylidene acetone; long-chain hydrocarbons; two-step hydrogenation/HDO process

Introduction
Recently intensive focus has been on the aqueous-phase processing for conversion of lignocellulosic biomass to liquid jet fuels, which developed a renewable route for bio-fuel production [1]. However, the aldol-condensation products from furan and acetone such as furfurylidene acetone (FA) and difurfurylidene acetone (F2A) are water-insoluble and unstable, which caused hydrogenation difficulty [2]. Two-step process of low-temperature hydrogenation (110-125°C) and the following high-temperature hydrodeoxygenation (HDO) for aldol-product conversion is usually utilized. Until now hydrogenation and HDO reactions are mostly carried out in tetrahydrofuran solvent (THF) over noble metal-based catalysts, especially for HDO where Pt/SiO2-Al2O3 was commonly used [3]. In this context Raney Ni and Pt/SiO2-ZrO2 were used as catalysts for two-step process of hydrogenation /HDO of F2A respectively.

Experimental section

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Raney Ni used was homemade and preserved in ethanol before use (Ni:Al=84.4:15.6, 
$S_{\text{BET}}=27.3\text{m}^2\cdot\text{g}^{-1}$, $\nu_{p}=0.03\text{cm}^3\cdot\text{g}^{-1}$, $d_p=4.5\text{nm}$). Pt/SiO$_2$-Al$_2$O$_3$ was prepared by incipient wetness impregnation of H$_2$PtCl$_6$·6H$_2$O on SiO$_2$-Al$_2$O$_3$ support with Si/Zr molar ratio of 3.0$^{[4]}$. Powder X-ray diffraction (XRD), NH$_3$-temperature programmed desorption (TPD) and thermal analysis(TG/DSC) were used for catalyst characterization. Low-temperature hydrogenation reaction was carried out in a batch reactor to produce hydrogenated intermediates(H-F$_2$A) under 2.5MPa. In each run, 8.0g of F$_2$A, 32ml solvent and 2.0g of catalyst were added to prepare 20wt.% F$_2$A solution. High-temperature HDO reaction was performed in a fixed-bed reactor. 4ml of 1wt.%Pt/SiO$_2$-Al$_2$O$_3$ was used and the typical operation conditions were $P=5.0\text{MPa}$, preheater temperature=150°C, flow rate of H-F$_2$A methanol solution=0.05ml/min with LHSV of 0.75h$^{-1}$.

**Results and discussion**

3.1 Low-temperature hydrogenation of F$_2$A

![Fig.1 Effect of solvent on low-temperature hydrogenation of F$_2$A over Raney Ni:](image)

(A)F$_2$A conversion as a function of time; (B) Selectivity of different H-F$_2$A intermediates at 2h TOS

Nine hydrogenated intermediates from F$_2$A hydrogenation in were detected by GC, shown in Fig.1, which could be sorted into three types of H-F$_2$A (type I: ketone H-dimers; type II: alcohol H-dimers; type III: spiro-H dimers) according to the hydrogenation degree of double bonds in F$_2$A. F$_2$A conversion in methanol(protic polar solvent), tetrahydrofuran(THF, aprotic polar solvent) and cyclo-hexane(nonpolar solvent) was 99.5%, 80.5% and 59.7% respectively, after 25min time on stream(TOS). The selectivity of deep hydrogenated intermediates of 1,5-bis(tetrahydrofuran-2-yl) pentan-3-ol(II-c) and 2-(2-(tetrahydrofuran-2-yl)ethyl)-1,6-dioxaspiro [4.4]nonane(III-b) was low, which was 19.0% and 10.0% in THF and cyclo-hexane respectively. Selectivity of II-c and III-b was as high as 80.8% at 2h TOS when methanol was used as F$_2$A solvent. The high selectivity of alcohol H-dimers and spiro-H dimers in methanol solvent may result from the protonation effect of methanol, which accelerated the activation of double bonds of alkene C=C, furan C=C and carbonyl C=O in F$_2$A molecule$^{[5]}$. And the H$_{ads}$, dissociated adsorbed on Raney Ni, was easy to saturate these functional groups.

**Table 1 The composition of H-F$_2$A under 5.0MPa and 50°C**

<table>
<thead>
<tr>
<th>Components*</th>
<th>I-a</th>
<th>I-b</th>
<th>I-c</th>
<th>I-d</th>
<th>I-e</th>
<th>II-a</th>
<th>II-b</th>
<th>II-c</th>
<th>III-a</th>
<th>III-b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>0.18</td>
<td>0.05</td>
<td>0.42</td>
<td>0.63</td>
<td>13.8</td>
<td>0.13</td>
<td>0.05</td>
<td>82.8</td>
<td>0.66</td>
<td>0.55</td>
</tr>
</tbody>
</table>

* The symbol represents the same component as in Fig.1.

Table 1 shows the components and contents in the hydrogenated intermediate liquid of H-F$_2$A after 2h TOS under H$_2$ pressure of 5.0MPa. Increasing H$_2$ pressure decreased selectivity of spiro-H dimers and increased II-c selectivity, which was 82.8%. It may be deduced that the C=C bonds in olefins and in furan ring were easier to be hydrogenated than C=O bonds in the furan rings. That promoted
selectivity of the primary hydrogenation product like ketone H-dimer of 1,5-di(tetrahydro-2-furanyl)-3-pentanone (I-e), which was further hydrogenated to II-c.

3.2 High-temperature HDO of H-F2A

The increase of initial H-F2A concentration decreased carbon alkane yield of C8-C14, which was 65.6% and 51.9% for 28wt.% and 38wt.% H-F2A solutions in table 2 respectively. And carbon yield of C13 decreased from 70.0% to 42.4%, which is the dominant product of HDO reaction. While carbon yields of unsaturated O-containing compounds increased, especially for 1-tridecanol. It may be due to the insufficient HDO capability over 1wt%Pt/SiO2-ZrO2 when high H-F2A contained feedstock was used.

<table>
<thead>
<tr>
<th>Concentration (wt.%)</th>
<th>Carbon alkane yield (%mol)</th>
<th>Yield of C8-C14 alkanes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2-C7</td>
</tr>
<tr>
<td>18</td>
<td>10.1</td>
<td>0.8</td>
</tr>
<tr>
<td>28</td>
<td>4.3</td>
<td>0.4</td>
</tr>
<tr>
<td>38</td>
<td>1.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Carbon alkane yield (%mol)</th>
<th>Yield of C8-C14 alkanes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2-C7</td>
</tr>
<tr>
<td>260</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>280</td>
<td>10.1</td>
<td>0.8</td>
</tr>
<tr>
<td>300</td>
<td>13.3</td>
<td>0.6</td>
</tr>
<tr>
<td>320</td>
<td>13.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Carbon yield of C8-C14 alkanes over 1wt%Pt/SiO2-ZrO2 was 40.5%, mainly of C13(33.6%) when HDO temperature was 260°C using 18wt.% H-F2A solution as feedstock in a fixed-bed reactor. 1-Tridecene, 1-tridecanol and 1-dodecanol were detected with carbon yield of 1-tridecanol as high as 11.7%, which indicates HDO reaction could not perform completely over 1wt%Pt/SiO2-ZrO2 at 260°C. As temperature was increased to 280°C, HDO performance was improved with clear and transparent liquid product, which naturally separated from methanol solvent. The carbon yield of 1-tridecanol was decrease to 0.9%. The carbon yield of long-chain alkanes of C8-C14 was 82.9%, including 70.0% to C13. Further increasing temperature to 300°C and 320°C, carbon yield of C8-C14 was decreased to 71.0% and 64.0% respectively.

HDO performance at over 1wt%Pt/SiO2-ZrO2 was operated for 120h. Carbon alkane yield of C8-C14 kept at 58.2-72.8% after 120h TOS at LHSV of 0.6h⁻¹. The stable activity of 1wt%Pt/SiO2-ZrO2 might deduce from its textural properties:(a) The acidic and basic centers of SiO2-ZrO2 support favoured activation of O-contained intermediates and decreased carbon deposition on the catalyst surface, as reported in guaiacol HDO reaction;(b)SiO2 with large surface area dispersed Pt active centers and ZrO2 for HDO reaction. Catalyst characterizations were performed to verify the deduction, shown in Fig.2. The fresh 1wt.%Pt/SiO2-ZrO2 shows NH3 desorption peak at 150-450°C, indicating the existing of weak and moderately strong acidity. After 120h HDO reaction, NH3-TPD pattern of the used 1wt.%Pt/SiO2-ZrO2 exhibits the decreased desorption area at 200-400°C with
increased desorption area above 400°C. That indicated the formation of stronger acid centers during HDO reaction\cite{6}, which might have activated O-containing intermediates to accelerate HDO reaction. While the similar XRD patterns of the used 1wt.%Pt/SiO_2-ZrO_2 in Fig.4.B indicated that stability of catalyst structure and active Pt phase during long time HDO operation. The weight loss of the used 1wt.%Pt/SiO_2-ZrO_2 with and without methanol washing was 7wt% and 32wt% respectively at 150-650°C. It is obvious that methanol solvent could dissolve and carry away the coke precursor to decrease carbon deposition\cite{7}, which had contributed to the stable performance of HDO over 1wt.%Pt/SiO_2-ZrO_2 in methanol solvent in this context.

![Graph A](A)  ![Graph B](B)  ![Graph C](C)

**Fig.4** Characterization patterns of 1wt.%Pt/SiO_2-ZrO_2. (A)NH_3-TPD; (B) XRD; (C)TG/DSC

### 4. Conclusion

Protonation effect of methanol solvent increased the low-temperature hydrogenation of F_2A and high-temperature HDO reactions of the hydrogenated H-F_2A compounds over Raney Ni and Pt/SiO_2-ZrO_2 catalysts respectively. And the stable HDO performance during 120h HDO reaction could be deduced from the stable structure properties and active centers over 1wt.%Pt/SiO_2-ZrO_2.

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### References


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