One-step hydrogenation–esterification of furfural and acetic acid over bifunctional Pd catalysts for bio-oil upgrading

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**A R T I C L E  I N F O**

Article history:
Received 22 April 2011
Received in revised form 2 June 2011
Accepted 4 June 2011
Available online 12 June 2011

Keywords:
Bio-oil upgrading
One-step hydrogenation–esterification
Bifunctional catalyst
Furfural
Acetic acid

**A B S T R A C T**

This contribution focuses on one-step hydrogenation–esterification (OHE) of furfural and acetic acid, which are difficult to treat and typically present in crude bio-oil, as a model reaction for bio-oil upgrading. A bifunctional catalyst is needed for OHE reaction. Among tested bifunctional catalysts, the 5%Pd/Al2(SiO3)3 shows the best catalytic performance. Compared to the physical mixture of 5%Pd/C + Al2(SiO3)3, there is a synergistic effect between metal sites and acid sites over 5%Pd/Al2(SiO3)3 for the OHE reaction. A moderate reaction condition would be required to obtain high yields of alcohol and ester along with lower byproduct yields. In this work, the optimum selectivity to desired products (alcohol and ester) of 66.4% is obtained, where the conversion of furfural is 56.9%. Other components, typically present in bio-oils, have little effects on the OHE of FAL and HAc. This OHE method is a promising route for efficient upgrading of bio-oil.

1. Introduction

With the declining of petroleum reserves and increasing of energy demand, as well as growing environmental concerns regarding fossil fuels, it is imperative to develop economical and energy-efficient processes for renewable transportation fuel and chemical production to supplement or replace those derived from petroleum (Corma et al., 2007; Huber et al., 2006; Simonetti and Dumesic, 2009). Biomass is deemed as the sustainable and renewable organic carbon substitute for petroleum (Klass, 1998). It is environment-friendly for its negligible sulfur, nitrogen, and ash content (resulting in low emissions of harmful pollutants), and for the greenhouse gas neutral property (with zero net carbon dioxide emission in virtue of photosynthesis). These advantages make biomass an excellent candidate for alternative energy source (Mckendry, 2002). Crude bio-oil is a liquid product from fast pyrolysis of biomass. Compared to biomass, bio-oil is convenient for storage and transportation and is adaptable to utilization of existing fuel distribution infrastructure. There are, however, many problems limiting bio-oil applications, such as poor volatility, low heating value, high viscosity, incompatibility with conventional fuels, coking, solid contents, corrosiveness, and chemical instability (Czernik and Bridgwater, 2004). The corrosiveness is caused by substantial amounts of organic acids, which result in a pH of 2–3. And the instability is due to considerable amounts of aldehydes, which are highly reactive for condensation and polymerization (Huber et al., 2006). Therefore, it must be upgraded if used as substitutes for diesel and gasoline fuels (Huber et al., 2006).

In the last two decades, techniques like hydro-deoxygenation (MERCADER et al., 2011; ŞENOL et al., 2005; ZHAO et al., 2011) and catalytic cracking (HEW et al., 2010; VITOTO et al., 2001; Xu et al., 2010; ZHANG et al., 2005) were widely used to upgrade crude bio-oil mainly in order to reduce the oxygen content. These techniques, requiring complicated equipment and excess cost, are usually halted by catalyst deactivation and reactor clogging. However, in order to improve fuel combustion characteristics it may be desirable to leave some of oxygen in the fuel (Huber et al., 2006). Apart from the above mentioned methods, there are also other atom-economic procedures in which oxygen does not necessarily need to be completely removed. The desired products can be combustible and stable oxygenous hydrocarbons such as esters and alcohols, in which, for example, esterification (Lilja et al., 2002; Marchetti et al., 2007; XIONG et al., 2009; ZHANG et al., 2006) and hydrogenation (MAHFUD et al., 2007; WANG et al., 2005) are basic processes.

**Abbreviations:** FAL, furfural (the reactant); HAc, acetic acid (the reactant); FOL, furfuryl alcohol (the hydrogenation product of FAL); FA, furfuryl acetate (the esterification product of FOL and HAc); MF, methyl furan (the hydrodeoxygenation product of FAL); BP, byproducts (the undesired products like polycondensation product); X;FAL, the conversion rate of FAL; Y(i), the yield to component i; S(i), the selectivity to component i; mFAL, in, the mass of furfural before reaction; mFAL, out, the mass of furfural after reaction; m(i), the mass of component i; M(i), the molecular weight of component i; i, FA, FOL, FA, MF or BP.

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These two processes have been researched separately, but few have combined them into one step for bio-oil upgrading.

The authors’ group focuses on treatment of acids and aldehydes which are two substantial organic constituents in bio-oils. In order to convert them to stable, combustible esters and alcohols, a novel upgrading method termed one-step hydrogenation–esterification (OHE) was established as a model reaction for upgrading of bio-oil (Tang et al., 2008). Since bio-oils are composed of a wide variety of oxygenated compounds, their upgrading is too complex to elucidate the reaction paths and the correlation between catalytic performances and catalyst’s structures. Reactions of model compounds can be utilized to deal with this complexity, and in our work, to help identifying the reactivity of acids and aldehydes species present in bio-oil thereby leading to the better design of OHE catalysts. In the previous papers, it is proved that the OHE reaction of acetaldehyde (and butyraldehyde) and acetic acid to ester is feasible over a bifunctional catalyst, such as 5%Pt/Al2(SiO3)3, 5%Pt/HZSM-5 or Pt/SBA15–PrSO4H (Tang et al., 2008, 2010). However, in crude bio-oil, the content of furfural (FAL) is higher than that of acetaldehyde or butyraldehyde; and furfural or other furan derivatives are very difficult to handle and are prone to deactivate catalysts significantly (Deng et al., 2009; Yang et al., 2010). Converting FAL is a necessary aspect to consider for bio-oil upgrading. The single hydrogenation of furfural to furfuryl alcohol (FOL) has been investigated extensively in the last several decades (Li et al., 2003, 2004, 2011). In the presence of acidic components, however, the FOL is prone to polymerization (Choura et al., 1996; Kijenski et al., 2002). Therefore, it is still quite a challenge to convert the active furfural in crude bio-oil to a stable compound.

In this work, the OHE reaction of furfural and acetic acid is studied, which has not been previously investigated. The novel OHE reaction of furfural and acetic acid as a model reaction for bio-oil upgrading is a promising route to meet the above mentioned challenge.

2. Methods

2.1. Materials

\[ \text{H}_2\text{PdCl}_4 \text{ and H}_2\text{PtCl}_6 \text{ solution (Hangzhou Kaiming Catalyst Co., Ltd., Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O (Sinopharm Chemical reagents Co., China), Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O (Sinopharm Chemical reagents Co., China), amorphous aluminum silicate (Sinopharm Chemical reagents Co., China, 170 m}^2/\text{g}), and activated carbon (coconut shell charcoal, China Tangshan Jianxin Activated Carbon Co., Ltd., 1020 m}^2/\text{g}) \text{ were employed to prepare the catalysts.} \]

Furfural, acetic acid and toluene, of analytical reagent, were purchased from Sinopharm Chemical reagents Co., and used as model compounds and solvent.

2.2. Catalyst preparation

The 5%Pd/C was prepared with the precipitation–reduction method. The activated carbon was pretreated with 2 mol/L nitric acid solution at 110 °C for 3 h and washed thoroughly with de-ionized water until the pH reached ca. 6.0, followed by drying at 110 °C overnight. A certain amount of the treated carbon was impregnated at room temperature with known concentrations of acidized H2PdCl4 solutions for 24 h and precipitated with 30 wt.% NaOH solution until the pH reached 9–10. Calculated amount of 1 wt.% hydrazine hydrate solution was added at 85 °C to reduce Pd2+ to Pd0. The substance was thoroughly washed until free of Cl− (tested with silver nitrate solution). The resulting catalyst was dried overnight at 60 °C in a vacuum oven.

The solid acid adopted in this work is amorphous Al2(SiO3)3. The mixed bifunctional catalyst adopted in this work is a physical mixture of 5%Pd/C and Al2(SiO3)3. It is designated as 5%Pd/C + Al2(SiO3)3, where 5% is the nominal weight percentage of metallic Pd.

The composite bifunctional catalyst used in this work is palladium loaded on acidic support of amorphous Al2(SiO3)3. It is denoted as 5%Pd/Al2(SiO3)3, where 5% is the nominal weight percentage of metallic Pd. The catalyst was also prepared with precipitation–reduction method by the following procedures. The support Al2(SiO3)3 was pretreated under air atmosphere at 550 °C for 2 h after that it was impregnated in certain volumes of diluted acidized H2PdCl4 solution at room temperature for 24 h. The Pd2+ was then precipitated on the support with 30 wt.% NaOH solution. A volume of 37 wt.% formaldehyde solutions was added at 85 °C to reduce Pd2+ to Pd0. The catalyst was washed thoroughly with de-ionized water until it was free from Cl− (tested with silver nitrate solution). The resulting catalyst was dried overnight at 60 °C in vacuo.

The preparation procedure of 5%Pt/Al2(SiO3)3, 5%Cu/Al2(SiO3)3 and 5%Ni/Al2(SiO3)3 is the same as that of 5%Pd/Al2(SiO3)3.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Rotaflex D/Max-C X-ray diffractometer using Cu Kα radiation at 40 kV and 120 mA. The Scherrer equation was then employed to estimate the Pd crystalline size of the catalysts. Transmission electron microscope (TEM) images were obtained on a JEM-200 transmission electron microscope. An accelerating voltage of 200 kV was adopted to observe the distribution of Pd particles on the supports.

CO chemisorption measurements were taken at 25 °C on a CHEMBET-3000 pulse flow system. Prior to measurements, samples were tablet formed, crushed and sieved to 40–60 mesh, heated at 10 °C/min under 30 mL/min of 5 vol.% H2/He up to 250 °C and held at the temperature for 1 h. After that, the samples were purged with 30 mL/min helium gas for 2 h at the same temperature. Finally, the catalysts were cooled down to 25 °C under He flow and CO pulses were introduced on the catalyst surface by using 5 vol.% CO in helium.

Inductively coupled plasma-mass spectroscopy (ICP-MS) was conducted on a PS1000 instrument from American LEEMAN LABS INC. to determine the real loading of Pd on the supports.

2.4. Catalytic activity evaluation

All the OHE reaction experiments were performed in a 100 mL stainless steel batch autoclave equipped with an electrical heating jacket and a mechanical overhead stirrer. The effect of mass transfer on catalytic performances was excluded (see supporting information, Fig. S1 and Fig. S2). For the stage of feasibility study in this work, the amount of FAL and HAc was not in accordance to the real ratio in bio-oils; in future work this factor will be taken into account. Typically, an equimolar mixture of 9.60 g FAL (0.10 mol) and 6.00 g HAc (0.10 mol) was dissolved in 10.0 mL toluene (Tol), added into the reactor, with 0.40 g catalyst (or 0.40 Pd/C + 0.40 g Al2(SiO3)3 for mixed bifunctional catalyst). Before each run, the autoclave was flushed five times with hydrogen to remove air from the setup. The reactor was connected to a hydrogen cylinder to maintain the inside pressure at an exact value (1.0–4.0 MPa). The mixture of substrates and catalyst was heated to a specific reaction temperature (80–200 °C) within half an hour. The stirring speed at 800 rpm and the particle size at smaller than 400 mesh were adopted to ensure that the catalytic performances were intrinsic. After some time of reaction (2–8 h), the reactor was cooled down in ice water to room temperature and the gas was released very slowly and collected into a gas bag that was purged with H2 five
The physical properties and related catalytic activities of the catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>X(FAL)</th>
<th>S(FOL)</th>
<th>S(FA)</th>
<th>S(MF)</th>
<th>S(BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5%Pd/Al2(SiO3)3</td>
<td>69.4</td>
<td>19.7</td>
<td>9.1</td>
<td>25.8</td>
<td>45.4</td>
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<tr>
<td>2</td>
<td>5%Pt/Al2(SiO3)3</td>
<td>41.2</td>
<td>35.0</td>
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<td>21.6</td>
<td>43.4</td>
</tr>
<tr>
<td>3</td>
<td>5%Pd/Al2(SiO3)3</td>
<td>18.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>4</td>
<td>5%Pd/Al2(SiO3)3</td>
<td>56.9</td>
<td>52.7</td>
<td>13.6</td>
<td>0.0</td>
<td>33.6</td>
</tr>
<tr>
<td>5</td>
<td>5%Pt/Al2(SiO3)3</td>
<td>50.2</td>
<td>53.2</td>
<td>13.5</td>
<td>0.0</td>
<td>34.7</td>
</tr>
<tr>
<td>6</td>
<td>5%Cu/Al2(SiO3)3</td>
<td>26.1</td>
<td>29.9</td>
<td>6.1</td>
<td>0.0</td>
<td>64.0</td>
</tr>
<tr>
<td>7</td>
<td>5%Ni/Al2(SiO3)3</td>
<td>23.9</td>
<td>25.9</td>
<td>5.0</td>
<td>0.0</td>
<td>69.0</td>
</tr>
</tbody>
</table>

*Reaction conditions: Tc = 150 °C, P0 = 2.0 MPa, 800 rpm, t = 4 h, 9.60 g FAL + 6.00 g HAc + 0.40 g Pd (or 0.40 g Pd/C + 0.4 g Al2(SiO3)3 in entry 1) in 10.0 mL Tol. FAL – furfural, HAc – acetic acid, Tol – toluene, FOL – furfuryl alcohol, FA – furfuryl acetate, MF – methyl furan, BP – byproducts.*

3. Results and discussion

3.1. Catalyst characterization results

3.1.1. XRD analysis

From X-ray diffraction patterns of 5%Pd/Al2(SiO3)3 and 5%Pd/C (not shown here), four peaks are observed at ca. 40.0°, 46.6°, 68.0° and 82.0°, which are ascribed to the characteristic diffraction peaks of crystal planes of metallic Pd (111), (200), (220) and (311), respectively (ICDD/JCPDS, PDF-# 65-2867). Besides, both catalysts exhibit a broad peak around 2θ = 26.5° and 2θ = 28.5° indicative of amorphous structure of Al2(SiO3)3 and activated carbon, respectively. No peaks of the Pd oxides are observed, demonstrating that the Pd species are primarily present in metallic form after reduction with formaldehyde (5%Pd/Al2(SiO3)3) or hydrazine (5%Pd/C). As summarized in Table 1, the mean crystalline diameter of Pd on 5%Pd/Al2(SiO3)3 is 15.6 nm and 16.4 nm, respectively. This illustrates that Pd particles are highly dispersed on these supports.

3.1.2. TEM characterization results

It can be learned from the size distributions of the supported Pd particles (calculated from the TEM images, not shown here) that the average diameter of Pd over Pd/Al2(SiO3)3 and Pd/C is 6.2 nm and 5.6 nm, respectively. This result is different from the Pd crystal size calculated from the Scherrer equation. It is because particles smaller than 5 nm cannot be detected in XRD characterization. The TEM images (not shown here) demonstrate that the particles of Pd on both 5%Pd/Al2(SiO3)3 and 5%Pd/C are smaller and highly dispersed, exhibiting a narrow size distribution.

3.1.3. ICP analysis results

The real Pd loadings of the 5%Pd/Al2(SiO3)3 and 5%Pd/C catalysts are listed in Table 1. The exact Pd loading of 5%Pd/Al2(SiO3)3 and 5%Pd/C is 4.9 wt.% and 3.7 wt.%, respectively. Both values are smaller than 5 wt.%, because the Pd2+ ion cannot be totally precipitated by sodium hydroxide and deposited on support. The Pd loading of 5%Pd/Al2(SiO3)3 is slightly higher than that of 5%Pd/C. This phenomenon may be related to the support property: In preparation of Pd/Al2(SiO3)3, when the Pd2+ was precipitated with sodium hydroxide, inevitably, support Al2(SiO3)3 was partly dissolved by NaOH, resulting in the real loading of Pd slightly higher but still lower than the nominal Pd loading.

3.1.4. CO chemisorption of 5%Pd/Al2(SiO3)3 and 5%Pd/C catalysts

The number of Pd sites on the supports (listed in Table 1) was estimated based on the CO chemisorption. The average stoichiometry of the Pd atom on the surface to the chemisorbed CO was reasonably assumed equal to 2 rather than 1 (Canton et al., 2002). The Dpd (dispersion of Pd) and dpd (diameter of Pd particle), also listed in Table 1, were calculated as reference (Aramendia et al., 1996). Although the Pd loading of 5%Pd/Al2(SiO3)3 (4.9 wt.%) is higher than that of 5%Pd/C (3.7 wt.%), the chemisorbed CO amount of 5%Pd/Al2(SiO3)3 is relatively smaller (Table 1), indicating that the dispersion of Pd on 5%Pd/Al2(SiO3)3 (20.4%) is lower than that of 5%Pd/C (28.2%). This may be attributed to the lower specific surface area of Al2(SiO3)3 compared to active carbon.

3.2. Catalytic Performances

3.2.1. The feasibility of OHE for FAL and HAc

The catalytic performances of the catalysts used for OHE reaction of FAL and HAc are listed in Table 2. In order to find out if it is possible that this reaction takes place over mixed bifunctional catalysts, this OHE reaction of FAL and HAc is conducted over a physical mixture of 5%Pd/C and Al2(SiO3)3. From entry 1, it is obvious that the OHE of FAL and HAc could be carried out over mixed bifunctional catalysts and some of the corrosive HAc and the unstable FAL were converted to stable and combustible FOL and FA. In addition, the hydrodeoxygenation product of methyl furan (MF) was found. In entry 2 over monofunctional 5%Pd/C, apart from FOL as the hydrogenation product of FAL, MF was also found as the over hydrogenation product of FAL. In entry 2 FA was not obtained for straightforward reason that the monofunctional 5%Pd/C catalyst did not have the function of esterification. Entry 3 shows that over monofunctional solid acid Al2(SiO3)3 no desired products are found owing to the fact that the intermediate FOL

Table 2

<table>
<thead>
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<th>X(FAL)</th>
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</tr>
<tr>
<td>2</td>
<td>5%Pd/C</td>
<td>41.2</td>
<td>35.0</td>
<td>0.0</td>
<td>21.6</td>
<td>43.4</td>
</tr>
<tr>
<td>3</td>
<td>C + Al2(SiO3)3</td>
<td>18.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>4</td>
<td>5%Pd/Al2(SiO3)3</td>
<td>56.9</td>
<td>52.7</td>
<td>13.6</td>
<td>0.0</td>
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</table>
cannot be obtained without the function of hydrogenation for Al_2(SiO_3)_3. The control experiments (Table S1, shown in supporting information) clearly indicate that furfuryl alcohol is the main product by the hydrogenation reaction, while furfuryl acetate is the esterified compound produced from furfuryl alcohol and acetic acid on acid sites. From entries 1–3, it is concluded that the OHE method of FAL and HAc is a feasible route for bio-oil upgrading. It must be conducted under the synergy of metal sites and acid sites.

It is well known that for cooperative catalysis the functional groups must be close enough to each other. So this OHE reaction of FAL and HAc is tested on a composite bifunctional catalyst of 5%Pd/Al_2(SiO_3)_3 (entry 4). By comparison of entry 3 and 4, it is known that both S(FOL) and S(FA) over 5%Pd/Al_2(SiO_3)_3 are higher than those over 5%Pd/C + Al_2(SiO_3)_3. In order to compare the activity of Pd sites on Al_2(SiO_3)_3 and activated carbon, the turnover frequency (TOF) under optimal conditions were calculated based on the conversion from FAL to the desired products of FOL and FA. The results are also listed in Table 1. It can be seen that the TOF of 5%Pd/Al_2(SiO_3)_3 (508.7 h^{-1}) is higher than that of 5%Pd/C (255.6 h^{-1}). Table 1 shows that the dispersion of Pd (20.4%) and the Pd content on the surface (4.884 ± 10^{-2} mmol/g), respectively. It is also shown in Table 1 that both d_{CD} (5.5 nm) and d_{TEM} (6.2 nm) of Pd on 5%Pd/Al_2(SiO_3)_3 is bigger than those on 5%Pd/C (4.0 nm, 5.6 nm), respectively. All these characterizations suggest that the hydrogenation activity of 5%Pd/C is superior to that of 5%Pd/Al_2(SiO_3)_3. Whereas, the catalytic activity for OHE reaction of 5%Pd/Al_2(SiO_3)_3 is better than that of 5%Pd/C + Al_2(SiO_3)_3. So, the activity of the catalysts for OHE is not correlated to the dispersion of metal particles. In addition, over physically mixed bifunctional catalysts (including Pd/C + HZSM-5, shown in supporting information, Table S2), the hydrodeoxygenation product of methyl furan was found, while no methyl furan was found over composite bifunctional catalyst. The better OHE performances over the composite bifunctional catalyst can be attributed to its better cooperative effect between metal sites and acid sites. To explain these phenomena, two different mechanisms were proposed for OHE reaction of FAL and HAc over physically mixed and composite bifunctional catalysts. As Fig. S4 shows, immediately after FAL being hydrogenated over metal sites to FOL, the in situ produced FOL reacts with HAc to form FA right over the acid sites of the 5%Pd/Al_2(SiO_3)_3, which can prevent the FOL from undergoing polycondensation reaction (supporting information, S3) to some extent. However, there are two possibilities in mixed bifunctional catalysts. On the one hand, because the acid sites and metal sites are distant, the overhydrogenation (hydrogenolysis) of FAL preferentially takes place to form methyl furan, as shown in Fig. S5. On the other hand, when there are acid sites in vicinity of metal sites, the produced FOL will react with HAc adsorbed on acid sites to form FA, like that shown in Fig. S4.

This OHE reaction of FAL and HAc is also tested on other bifunctional catalysts (entries 5–7); the desired products of FOL and FA are produced. It is found that the selectivity to ester is dependent

![Fig. 1](image-url)
on the hydrogenation activity of the bifunctional catalysts. As shown in entries 4 and 5, the Al₂(SiO₃)₃ supported noble metals possess higher activity for hydrogenation of FAL, hence obtain relatively higher ester yield. Entries 6 and 7 demonstrate that the Al₂(SiO₃)₃ supported transition metals possess relatively poor activity for hydrogenation of FAL, therefore, lower selectivity to ester is obtained. The support for the bifunctional catalysts is preliminarily screened. Weak acid sites of the supports seem to favor the formation of furfuryl acetate (Table S2).

It is concluded that the OHE of furfural and acetic acid is feasible over bifunctional catalysts that possess indispensable functions of both hydrogenation and esterification. It is a potential method for catalytic upgrading of bio-oil. It would be desirable to develop a kind of catalyst that possesses high activity for hydrogenation and esterification at mild reaction conditions, so that the side reaction could be limited at minimum.

3.2.2. Effects of reaction conditions on OHE of FAL and HAc

The effects of reaction conditions on OHE reaction of FAL and HAc were examined over 5%Pd/Al₂(SiO₃)₃ catalyst. It could be learned from Fig. 1 (detailed discussions are shown in supporting information, S7) that higher temperature and longer reaction time are favorable for the side reaction of FOL polycondensation, and that a large amount of catalyst leads to superabundant acid sites which can also catalyze FOL condensation and make byproduct formation more competitive than ester (FA). An increase in H₂ pressure reduces the selectivity to FOL and hence to FA (due to the overhydrogenation of the FAL to tetrahydrofurfuryl alcohol or the hydrodeoxygenation of FAL to methyl furan), and this results in the unnecessary consumption of hydrogen. A moderate reaction condition would be required to obtain high yields of ester and alcohol along with lower byproduct yields. In this work, the optimal reaction conditions are: \( T = 150 \, ^\circ\text{C}, \, P_{\text{H}_2} = 2.0 \, \text{MPa}, \, 800 \, \text{rpm}, \, m_{\text{cat}} = 0.40 \, \text{g (9.60 g FAL and 6.00 g HAc in 10.0 mL toluene)}, \, t_R = 4 \, \text{h}. \) Under these conditions, the conversion of FAL is 56.9%, and the selectivity to desired products reach to 66.4% \( \text{(S\text{(FOL)} = 52.8\%, \text{S\text{(FA)} = 13.6\%).} \)

3.2.3. Effects of other typical bio-oils components on OHE of FAL and HAc

The influences of other components typically present in bio-oils were examined in order to check its viability for improving the quality of bio-oils. Phenol, acetone, ethanol, butyraldehyde and ethyl acetate were added to the feedstock (0.10 mol FAL, 0.10 mol HAc in 10.0 mL toluene), respectively. The results are listed in Table 3. Though some side reactions take place, the OHE reaction is the dominant process, with alcohols and esters as the desired products. The results for adding each component are described as follows:

(1) As 0.10 mol phenol was added to the reactant system, no phenol was converted. Interestingly, the addition of phenol increased the conversion of FAL without leading to the increase in desired product yields (FOL and FA). Therefore, the addition of phenol is suggested to favor some side reactions of the furfural. Detailed mechanisms need further investigation.

(2) When 0.10 mol acetone was added to the reactant mixture, the conversion of FAL increased, but the yields to FOL and FA did not change evidently. The aldol condensation products were found in the byproducts.

(3) Using 0.10 mol butyraldehyde and 0.10 mol HAc in 10.0 mL toluene as feedstock, the case was somewhat complicated. Apart from FOL and FA, the products of butanol and butyl acetate were also observed. This indicates that the OHE of butyraldehyde and acetic acid also takes place and it competes with OHE of FAL and HAc. Meanwhile the aldol condensation products were found in the byproducts as well.

(4) The addition of 0.10 mol ethanol to the reactant mixture was also investigated. On the one hand, it favors the hydrogenation of FAL to FOL, which maybe because it is easier for ethanol to dissolve furfural and hydrogen. On the other hand, ethanol competes with FOL to react with HAc, lowering the yield of FA.

(5) When 0.10 mol ethyl acetate was added to the feedstock (0.10 mol FAL and 0.10 mol HAc in 10.0 mL toluene), the total yields of desired products (FOL and FA) were not changed, with increase of the yield of FA and decrease of the yield of FOL.

Thus, the selectivity for desired products (FOL and FA) decreases to some extent when phenol, acetone, butyraldehyde, ethanol and ethyl acetate are present (a decrease of 18.8%, 25.9%, 29.4%, 5.3% and 14.6%, respectively), and the selectivity of byproducts (resulting from polycondensation) increases accordingly. In a word, this OHE method shows promising viability for improving the quality of bio-oils, although other components that are typically present in bio-oils have some negative effects on the OHE reaction of FAL and HAc. A following challenge involves improving the conversation of FAL and the selectivity towards FA and FOL, decreasing byproduct yield. Future work plans to carry out this OHE reaction using real bio-oil as a feedstock to check the utility of this method for bio-oil upgrading. The ultimate goal is the design of a bifunctional or multifunctional catalyst which can convert various corrosive nonflammable acids and reactive unstable aldehydes in bio-oils to stable and combustible esters and alcohols with high activity and selectivity.

4. Conclusions

The conclusions are drawn as follows: (1) The OHE of furfural and acetic acid is feasible over composite or physically mixed bifunctional catalysts. It is a promising method for catalytic upgrading of bio-oil. (2) There is a better synergistic effect of metal sites and acid sites for the OHE reaction over composite bifunctional catalyst of 5%Pd/Al₂(SiO₃)₃. (3) A moderate reaction condition would be required to obtain high yields of alcohol and ester along with lower byproduct yields. (4) Other components, typically present in bio-oils, have some little effects on the OHE of FAL and HAc.

Acknowledgement

Financial support from the National Basic Research Program of China (2007CB210204) is gratefully acknowledged.

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Table 3

<table>
<thead>
<tr>
<th>Component added</th>
<th>X(FAL) (%)</th>
<th>X(FOL) (%)</th>
<th>X(FA) (%)</th>
<th>X(D) (%)</th>
<th>X(BP) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>52.8</td>
<td>56.8</td>
<td>14.6</td>
<td>71.4</td>
<td>28.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>61.7</td>
<td>45.2</td>
<td>12.8</td>
<td>58.0</td>
<td>42.0</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>69.0</td>
<td>41.3</td>
<td>11.6</td>
<td>52.9</td>
<td>47.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>67.6</td>
<td>40.5</td>
<td>9.9</td>
<td>50.4</td>
<td>49.6</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>59.3</td>
<td>58.5</td>
<td>9.1</td>
<td>67.6</td>
<td>32.4</td>
</tr>
</tbody>
</table>

* Reaction conditions: \( T = 150 \, ^\circ\text{C}, \, P_{\text{H}_2} = 2.0 \, \text{MPa}, \, 800 \, \text{rpm}, \, t_R = 4 \, \text{h}, \, 9.60 \, \text{g (0.10 mol) FAL} + 6.00 \, \text{g (0.10 mol) + 0.40 g Pd/Al₂(SiO₃)₃}, \, \text{HAc in 10.0 mL Tol. FAL} – \, \text{furfural, HAc} – \, \text{acetic acid, Tol} – \, \text{toluene, FOL} – \, \text{furfuryl alcohol, FA} – \, \text{furfuryl acetate, D} – \, \text{desired products (FOL + FA), BP – byproducts.} \)
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2011.06.015.

References


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