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# One-Step Hydrogenation–Esterification of Aldehyde and Acid to Ester over Bifunctional Pt Catalysts: A Model Reaction as Novel Route for Catalytic Upgrading of Fast Pyrolysis Bio-Oil

Yang Tang, Wanjin Yu, Liuye Mo,\* Hui Lou, and Xiaoming Zheng\*

*Institute of Catalysis, Zhejiang University, Hangzhou 310028, P. R. China*

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The bio-oil from fast pyrolysis of biomass cannot be used effectively as engine fuel because of its high corrosiveness and instability mainly due to substantial amounts of organic acids and reactive aldehydes. In this paper a treatment of acids and aldehydes in the bio-oil was focused on. A novel upgrading method named one-step hydrogenation–esterification (OHE) was established to convert acids and aldehydes to stable and combustible components. Acetaldehyde (butyl aldehyde) and acetic acid were chosen as model compounds for the OHE reaction over platinum catalysts that acidic supports such as HZSM-5 or amorphous aluminum silicate were adopted. The catalysts were bifunctional, which means they have properties of hydrogenation and esterification. Experiments showed this, and it was a feasible route to convert these main unstable components of bio-oil to esters through this simple and effective OHE reaction. The catalysts with high surface area, large pore size distribution, small metal particles, and strong acid sites may be beneficial for the OHE reaction.

## Introduction

With increasing energy demand and exhausting fossil fuels, it is imperative to explore substitutes which are renewable, sustainable, and environmentally benign. Biomass, which stores solar energy through photosynthesis, is renewable and available in huge amounts. It is clean for its negligible content of sulfur, nitrogen, and ash, which give lower emissions of harmful pollutants than conventional fossil fuels. It is also greenhouse gas neutral because the CO<sub>2</sub> emitted from fuels is recycled by photosynthesis. All these advantages make biomass a potential alternative energy source.<sup>1–4</sup>

Among various energy forms, liquid fuels are convenient for storage and transportation and are conducive to existing fuel distribution infrastructure. In addition, biomass fast pyrolysis liquefaction is becoming an increasingly attractive research topic.<sup>5,6</sup> The liquid product from biomass pyrolysis is named as biomass pyrolysis oil or bio-oil for short. The compositions of bio-oil vary considerably with reportedly more than 400 organic compounds mainly composed of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, and components with multifunctional groups.<sup>7</sup> Bio-oil has deleterious properties with high oxygen content (35–40%), low heating value, corrosiveness, high viscosity, incomplete volatility, and chemical instability.<sup>8</sup>

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.<sup>1</sup> Therefore, bio-oil cannot be used effectively as engine fuel unless it is upgraded to be more combustible and more stable for long-time storage and transportation.

Presently, bio-oil upgrading techniques include hydrodeoxygenation,<sup>9–14</sup> catalytic cracking,<sup>15–18</sup> and steam reforming<sup>19,20</sup> mainly in order to reduce the oxygen content. But these techniques need complicated equipment and excess cost and usually are halted by catalyst deactivation and reactor clogging. Apart from these methods, there are also other atom-economic methods in which oxygen does not necessarily need to be removed totally. The aim products can be combustible and stable oxygenous hydrocarbons such as esters and alcohols, in which, for example,

\* To whom correspondence should be addressed. Fax: +86-571-88273283. E-mail: moliuye@zju.edu.cn (L.Y.M.); xmzheng@zju.edu.cn (X.M.Z.)

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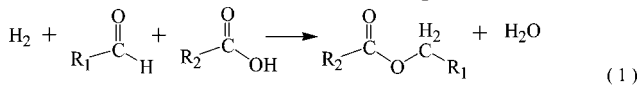
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esterification and hydrogenation are basic processes.<sup>21–26</sup> Much research<sup>23,26</sup> has been done for these two processes, but few have combined them into one step for bio-oil upgrading.

This paper focuses on a treatment of acids and aldehydes which are two main distinguishing organic components in the bio-oil. To convert them to stable and combustible esters, a novel upgrading method called one-step hydrogenation–esterification (OHE) was established as a model reaction for upgrading of bio-oil. The aim reaction is shown in eq 1.



It was catalyzed by model bifunctional catalysts with platinum loaded on acidic supports such as HZSM-5 or amorphous aluminum silicate. The experiments demonstrated the feasibility of converting the two main unstable components in the bio-oil to esters in the OHE reaction which may be a simple, effective and new approach for bio-oil upgrading. It was used to simulate the reactivity of aldehydes and acids in the bio-oil.

## Experimental Section

**1. Catalysts Preparation.** The catalysts used in these experiments were bifunctional, which loaded platinum on acidic supports such as HZSM-5 (Si/Al = 70, Shanghai Huaheng Chemical Co. Ltd.) or amorphous aluminum silicate (Sinopharm Chemical reagents Co., China). Two catalysts were designated as 5%Pt/HZSM-5 and 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>, respectively, where 5% was the weight percentage of Pt. The catalysts were prepared with incipient wetness impregnation by the following procedures. At first, support was impregnated in certain volumes of diluted chloroplatinic acid solution for 24 h and dried at 110 °C for 4 h (typically 0.8 mL of solution per gram support for 5%Pt/HZSM-5 and 1 mL of solution per gram support for 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>). Then in H<sub>2</sub> atmosphere, the catalyst was heated with a ramp of 7 °C/min and maintained at 360 °C for 1 h to reduce Pt<sup>6+</sup> to Pt<sup>0</sup>.

**2. Catalytic 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. For OHE reaction of acetaldehyde and acetic acid, the reactants were an aqueous solution of acetaldehyde (30 g, 40 wt %) and acetic acid (16 g). For the OHE reaction of butyl aldehyde and acetic acid, the reactants were butyl aldehyde (18 g) and acetic acid (15 g). A total of 0.2 g of catalyst was used in the catalytic reaction. The autoclave was flushed three times with hydrogen to remove oxygen from the setup, and the stirring speed was 750 rpm. After the reactor was heated to the reaction temperature of 150 °C, hydrogen was continuously added until the pressure inside the reactor was increased to 15 atm. After a 4 h reaction, the hydrogen was released and the reactor content was cooled down to room temperature. The products were analyzed with a gas chromatogram equipped with a flame ionization detector (FID) and a PEG-20000/GDX-103 polar column. All the reaction conditions followed the above procedures unless otherwise stated.

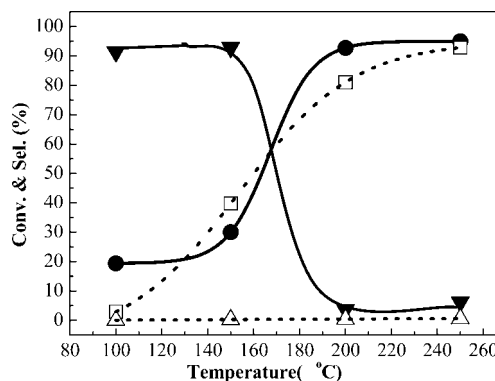
**3. Catalyst Characterization.** The X-ray diffraction analysis (XRD) was performed on a XRD powder diffractometer (D/MAX-RB, Japan) by using Cu Kα radiation at 40 kV and 120 mA. Then the Scherrer equation was used to estimate the Pt crystal size over the catalysts.

The specific surface areas and pore size distributions of the catalyst samples were determined by a standard BET technique with N<sub>2</sub> adsorption on an automated adsorption apparatus (OMNISORP 100CX). All samples were pretreated in a high vacuum at 195 °C

**Table 1. Blank Experiments and Catalytic Evaluation of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and 5%Pt/HZSM-5<sup>a</sup>**

catalyst	C <sub>A</sub> <sup>b</sup> (%)	selectivity <sup>c</sup> (%)			C <sub>B</sub> <sup>d</sup> (%)	selectivity <sup>e</sup> (%)		
		EA	ET	BP		BA	BU	BP
blank	6.7	7.5	1.5	91.0	39.7	0.3	0	99.7
5%Pt/HZSM-5	17.4	39.7	3.4	56.9	73.8	7.2	1.6	91.2
5%Pt/Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub>	23.5	71.9	20.4	7.7	30.0	93.0	0.3	6.7

<sup>a</sup> Reaction conditions: T<sub>r</sub> = 150 °C, P<sub>H</sub> = 15 atm, catalyst amount is 0.2 g, reaction time is 4 h, stirring speed is 750 rpm. <sup>b</sup> Conversion of acetaldehyde (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = CH<sub>3</sub>, R' = H). <sup>c</sup> EA, ethyl acetate; ET, ethanol; BP, byproduct. <sup>d</sup> Conversion of butyl aldehyde (R<sub>1</sub> = CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–, R<sub>2</sub> = CH<sub>3</sub>, R' = CH<sub>3</sub>–CH<sub>2</sub>–). <sup>e</sup> BA, butyl acetate; BU, butanol; BP, byproduct.



**Figure 1.** Effect of reaction temperature on the OHE reaction over 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>. (□) conversion of butyl aldehyde in blank experiments; (Δ) selectivity to butyl acetate in blank experiments; (●) conversion of butyl aldehyde in catalytic experiments; (▼) selectivity to butyl acetate in catalytic experiments. (Conditions are constant: P<sub>H</sub> = 15 atm, catalyst amount is 0.2 g, reagent amounts are 18 g of butyl aldehyde and 15 g of acetic acid, reaction time is 4 h, stirring speed is 750 rpm.)

for 2 h. The pore size distributions were calculated using the Barret–Joyner–Hallenda (BJH) method on the desorption branch.

Transmission electron microscopy (TEM) images were obtained on a JEM-200 transmission electron microscope. An accelerating voltage of 200 kV was adopted to observe the distribution of Pt particles on the supports.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) measurements were carried out to determine the amount and relative strength of acid sites. Typically 0.1 g of a sample was employed. The sample was pretreated at 300 °C in a flow of He (20 mL/min) for 1 h and adsorbed a flow of NH<sub>3</sub> (5% in N<sub>2</sub>, 20 mL/min) at room temperature for 1 h, and then it purged with He until the physically sorpted NH<sub>3</sub> was removed. The sample was then heated under a flow of He (20 mL/min) from room temperature to 800 °C with a ramp of 7 °C/min. The signals of NH<sub>3</sub>-TPD were recorded with an online thermal conducted detector (TCD) after the effluent gas was dried by solid CaO.

## Results and Discussion

**1. Catalytic Evaluation Results.** Table 1 displays the OHE reaction results with the presence of bifunctional platinum catalysts and absence of catalyst (blank experiment). The blank experiments showed low yields of esters, 0.5% for ethyl acetate (EA) and 0.3% for butyl acetate (BA), but high yields > 91% of byproducts (formed as eq 2) both from acetaldehyde and butyl aldehyde. The yields of esters significantly rose with the presence of bifunctional platinum catalysts. However, the yields

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of esters were 16.9% for EA and 27.9% for BA over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst, which were higher than the yields over the 5%Pt/HZSM-5 catalyst (6.9% for EA and 5.3% for BA). Interestingly, the conversion of butyl aldehyde (C<sub>B</sub>) was suppressed as the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst was presented. However, the C<sub>B</sub> was greatly accelerated from 39.7% to 73.8% with the presence of 5%Pt/HZSM-5 catalyst.

Figure 1 shows the effects of reaction temperature (*T<sub>r</sub>*) on the OHE reaction between butyl aldehyde and acetic acid over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst. In blank experiments, the C<sub>B</sub> increased from 2.9% to 92.8% with the *T<sub>r</sub>* increasing from 100 to 250 °C, but the selectivity to ester (*S<sub>E</sub>*) did not significantly go up with the *T<sub>r</sub>* increasing. In catalytic reactions over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst, the C<sub>B</sub> increased from 19% at 100 °C to 95% at 250 °C, but the *S<sub>E</sub>* decreased from ~92% at *T<sub>r</sub>* < 150 °C to ~6% at *T<sub>r</sub>* > 200 °C. It was demonstrated that bio-oil is reactive without catalyst due to the unstable aldehydes under acidic conditions at high temperatures. Low temperature is needed for the OHE reaction to avoid the formation of byproducts probably caused by the condensation reaction of aldehydes (shown as eq 2).

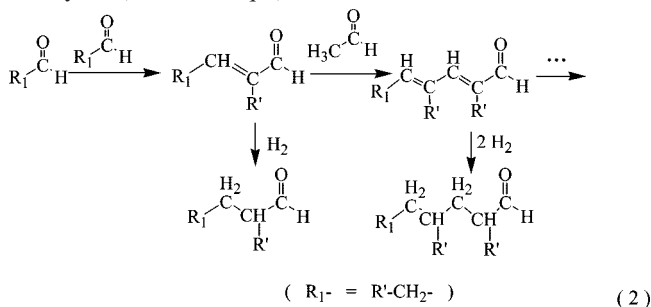
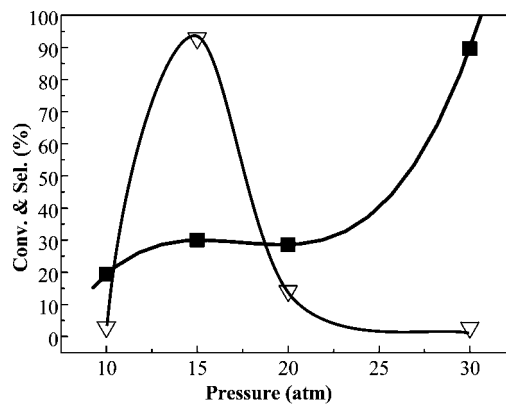


Figure 2 depicts the effects of hydrogen pressure (*P<sub>H</sub>*) on the OHE reaction of butyl aldehyde and acetic acid over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst. The C<sub>B</sub> increased from 19% to 89% while increasing the *P<sub>H</sub>* from 10 to 30 atm. However, the *S<sub>E</sub>* increased from 3% to a maximum (92%) with the *P<sub>H</sub>* increasing from 10 to 15 atm and then decreased to 3% at 30 atm.

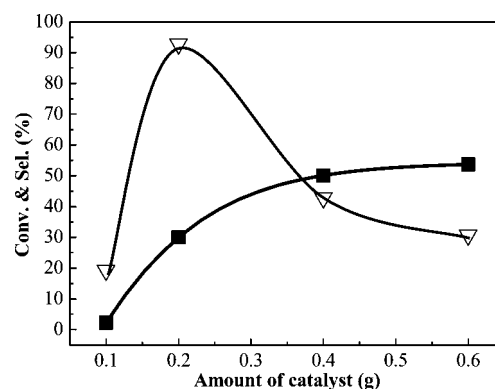
The effects of the catalyst amount on the OHE reaction between butyl aldehyde and acetic acid was also investigated over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> catalyst (shown in Figure 3). The reagent amounts were constant at 18 g of butyl aldehyde and 15 g of acetic acid. The C<sub>B</sub> rose from 2% to 54% with the catalyst amount increasing from 0.1 to 0.6 g, but the *S<sub>E</sub>* increased to a maximum (92% at 0.2 g) and then dropped to 30% at 0.6 g.

It could be learned from above experiment results that high temperature and high hydrogen pressure are favorable for the condensation reaction of aldehydes, and a large amount of catalyst leads to superabundant acid sites which can also catalyze aldehyde condensation and make byproduct formations more competitive than esters. Moderate reaction conditions should be applied to obtain the highest yield of esters and the lowest yield of byproducts such as those through aldehyde condensation. As Table 1 shows, at the optimum conditions, the difference of the conversions of acetaldehyde and butyl aldehyde may be due to the different suitable conditions for their conversions (including two parallel processes as hydrogenation and condensation) and may also be due to the different properties of the two catalysts shown in the characterization results.

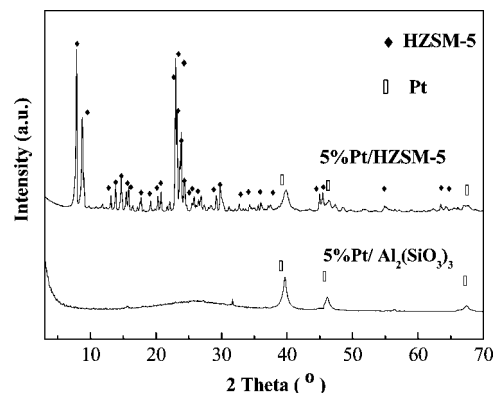
**2. Catalyst Characterization Results.** The X-ray diffraction patterns of 5%Pt/HZSM-5 and 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> are shown in Figure 4. The main peaks of the XRD patterns of 5%Pt/HZSM-5 were consistent with the characteristic peaks of HZSM-5, showing that the framework of the HZSM-5 support was not destroyed during the preparation procedures. The characteristic



**Figure 2.** Effect of hydrogen pressure on the OHE reaction over 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>. (■) Conversion of butyl aldehyde; (▽) selectivity to butyl acetate. (Conditions are constant: *T<sub>r</sub>* = 150 °C, catalyst amount is 0.2 g, reagent amounts are 18 g of butyl aldehyde and 15 g of acetic acid, reaction time is 4 h, stirring speed is 750 rpm.)



**Figure 3.** Effect of catalyst amount on the OHE reaction over 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>. (■) Conversion of butyl aldehyde; (▽) selectivity to butyl acetate. (Conditions are constant: *T<sub>r</sub>* = 150 °C, *P<sub>H</sub>* = 15 atm, reagent amounts are 18 g of butyl aldehyde and 15 g of acetic acid, reaction time is 4 h, stirring speed is 750 rpm.)



**Figure 4.** XRD patterns of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and 5%Pt/HZSM-5.

peaks for Pt metal were detected for all the samples, and no peaks of the platinum oxides were observed, demonstrating that the Pt species were mainly in the form of metal after prereduc-tion with hydrogen. The Pt crystalline sizes, calculated from the Scherrer equation, are listed in Table 2. The crystalline diameter of Pt on the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> was 12.6 nm, while that of the 5%Pt/HZSM-5 was 33.6 nm.

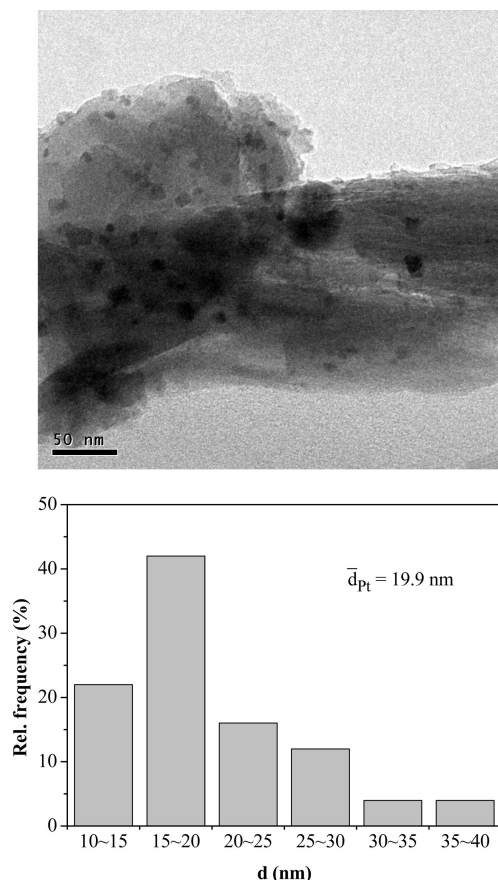
Figures 5 and 6 show the TEM images of the fresh catalyst samples and the size distributions of the supported Pt particles, which were calculated from the TEM images. The average particle size of Pt was smaller (about 6.9 nm) than that on 5%Pt/HZSM-5 (about 19.9 nm). This result was different from the



**Table 2. Partial Results of Catalyst Characterization of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and 5%Pt/HZSM-5**

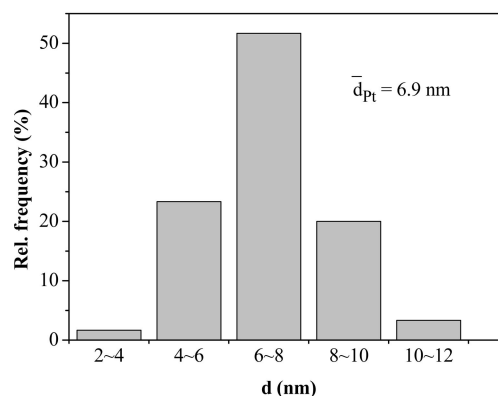
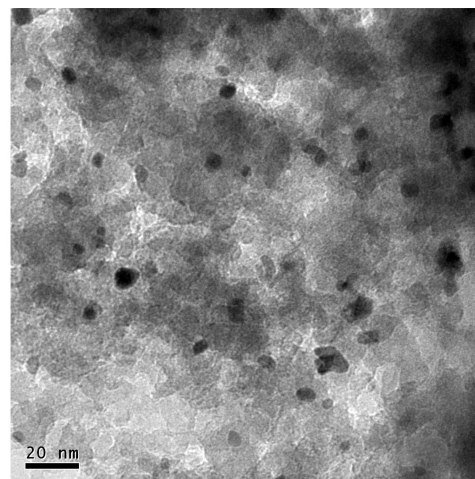
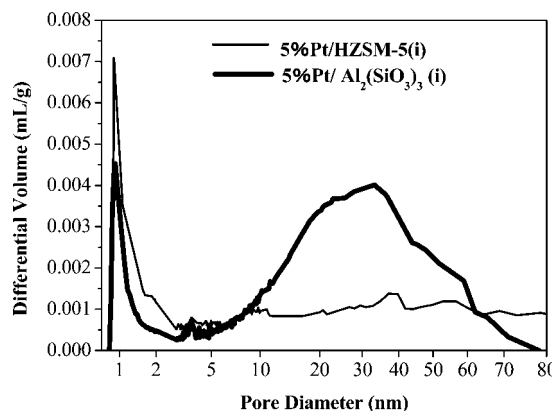
catalyst	surface area <sup>a</sup> (m <sup>2</sup> /g)	average particle diameter of Pt <sup>b</sup> (nm)	total acid sites <sup>c</sup> (μmol NH <sub>3</sub> /g)
5%Pt/HZSM-5	137	33.6	15.5
5%Pt/Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub>	160	12.3	19.6

<sup>a</sup> BET surface area from N<sub>2</sub> adsorption results. <sup>b</sup> Average particle diameter of Pt calculated from XRD. <sup>c</sup> Calculated from the peak areas of the NH<sub>3</sub>-TPD profiles and calibrated by a standard curve.

**Figure 5.** TEM image of the fresh catalyst sample of 5%Pt/HZSM-5 and size distribution of the supported Pt particles.

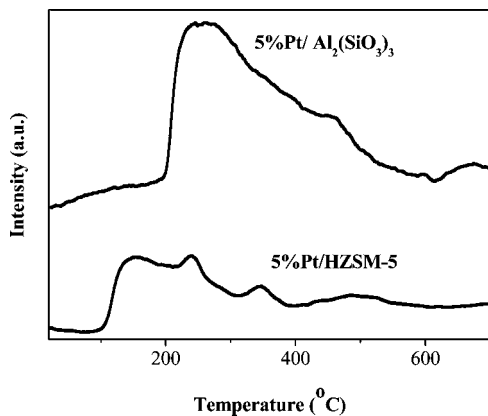
Pt crystalline sizes calculated from the Scherrer equation, but it also demonstrated that the particles of Pt on 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> were smaller and highly dispersed and exhibited a narrow size distribution. Therefore, the micropores of HZSM-5 might not be beneficial to the dispersion of Pt with the incipient wetness impregnation method. Also it was always considered that the higher dispersion leads to the higher activity for a reaction. Thus, a high dispersion of Pt might be beneficial to the OHE reaction.

The results of the surface area and pore distribution are shown in Table 2 and Figure 7. It shows that the surface area of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> was 160 m<sup>2</sup>/g, which was higher than 5%Pt/HZSM-5 (137 m<sup>2</sup>/g). The 5% Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> had more mesopores ranging from 10 to 60 nm, and the most probable distribution was located at ~30 nm, but HZSM-5 was a microporous zeolite. Larger pore volume can lead to higher surface area, and higher surface area may favor the higher dispersion of Pt so as to improve hydrogenation activity. It could be deemed that the surface area and pore size of the support were important factors for the OHE reaction. Higher yield of esters over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> than that over 5%Pt/HZSM-5 (Table 1) could be explained by the above reasons. The mesopore is very important for a reaction, especially for the reaction of large molecules that is abundant in the real bio-oil system. Thus, a mesoporous

**Figure 6.** TEM image of the fresh catalyst sample of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and size distribution of the supported Pt particles.**Figure 7.** Pore size distributions of 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and 5%Pt/HZSM-5.

material might be a good candidate for the process of catalytic upgrading bio-oil.

The profiles of NH<sub>3</sub>-TPD to characterize acidic properties of 5%Pt/HZSM-5 and 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> are shown in Figure 8. The NH<sub>3</sub> desorption temperature (*T<sub>D</sub>*) over the 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> appeared between ~200 °C and ~600 °C, which was higher than that over the 5%Pt/HZSM-5 (between ~100 °C and ~600 °C). This suggested that the strength of acidic sites over 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> was stronger than that over 5%Pt/HZSM-5. Furthermore, the amounts of acidic sites over 5%Pt/Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub> and 5%Pt/HZSM-5 were 19.6 and 15.5 μmol NH<sub>3</sub>/g (shown in Table 2). The acidic property of a catalyst is a key factor for an esterification reaction. In addition, it is reasonable to deduce



**Figure 8.**  $\text{NH}_3$ -TPD profiles of 5%Pt/ $\text{Al}_2(\text{SiO}_3)_3$  and 5%Pt/HZSM-5. that stronger acidic strength might be an important factor for the high yield of ester over the Pt bifunctional catalyst.

### Conclusions

The OHE reaction between aldehyde and acid to ester is feasible over a bifunctional catalyst. It is a potential route to be

used in the catalytic upgrading of fast pyrolysis bio-oil. The bifunctional catalyst of 5%Pt/ $\text{Al}_2(\text{SiO}_3)_3$  has a higher activity for ester formation than that of 5%Pt/HZSM-5. This result is probably due to its higher surface area, larger pore diameter, smaller size of metal particle, and stronger acid sites. In the future research, the catalytic activity of OHE reaction should be improved, and more suitable routes and catalysts applied to the catalytic upgrading of fast pyrolysis bio-oil should be explored.

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**Supporting Information Available:** More details about the effect of reaction time and the results of hydrogenation and esterification individually. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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