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

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ABSTRACT

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/$Al_2(SiO_3)_3$ shows the best catalytic performance. Compared to the physical mixture of 5%Pd/C + $Al_2(SiO_3)_3$, there is a synergistic effect between metal sites and acid sites over 5%Pd/$Al_2(SiO_3)_3$ 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; Vitolo 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; m(FAL, in), the mass of furfural before reaction; m(FAL, out), the mass of furfural after reaction; m (i), the mass of component i; M (i), the molecular weight of component i; i, FAL, 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/$Al_2(SiO_3)_3$, 5%Pt/HZSM-5 or Pt/SBA15–$PrSO_3H$ (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; Kijeński 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

H_2PdCl_4 and H_2PtCl_6 solution (Hangzhou Kaiming Catalyst Co., Ltd.), $Ni(NO_3)_2 \cdot 6H_2O$ (Sinopharm Chemical reagents Co., China), $Cu(NO_3)_2 \cdot 3H_2O$ (Sinopharm Chemical reagents Co., China), amorphous aluminum silicate (Sinopharm Chemical reagents Co., China, 170 m^2/g), and activated carbon (coconut shell charcoal, China Tangshan Jianxin Activated Carbon Co., Ltd., 1020 m^2/g) 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 H_2PdCl_4 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 Pd^{2+} to Pd^0. 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 $Al_2(SiO_3)_3$. The mixed bifunctional catalyst adopted in this work is a physical mixture of 5%Pd/C and $Al_2(SiO_3)_3$. It is designated as 5%Pd/C + $Al_2(SiO_3)_3$, 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 $Al_2(SiO_3)_3$. It is denoted as 5%Pd/$Al_2(SiO_3)_3$, 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 $Al_2(SiO_3)_3$ was pretreated under air atmosphere at 550 °C for 2 h after that it was impregnated in certain volumes of diluted acidized H_2PdCl_4 solution at room temperature for 24 h. The Pd^{2+} 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 Pd^{2+} to Pd^0. 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/$Al_2(SiO_3)_3$, 5%Cu/$Al_2(SiO_3)_3$ and 5%Ni/$Al_2(SiO_3)_3$ is the same as that of 5%Pd/$Al_2(SiO_3)_3$.

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.% H_2/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 $Al_2(SiO_3)_3$ 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 H_2 five