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# Vapor-phase hydrodeoxygenation of lignin-derived bio-oil over Al-MCM-41 supported Pd-Co and Pd-Fe catalysts

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#### ABSTRACT

Fast pyrolysis of lignocellulosic biomass is an attractive process to produce bio-oil as an alternative liquid fuel source. Upgrading of bio-oil via hydrodeoxygenation (HDO) is an important route to accomplish this renewable energy production process. Al-MCM-41 supported Pd, Co and Fe catalysts were evaluated for HDO of guaiacol and lignin-derived bio-oil at atmospheric pressure in a fixed-bed reactor. Bimetallic Pd-Co and Pd-Fe catalysts showed higher HDO yield and stability than the monometallic Co and Fe catalysts. The addition of Pd significantly enhanced the stability of Co and Fe catalysts since it helped reduce the coke formation. The lignin-derived bio-oil mainly contained phenolic compounds which had one to three oxygen atoms. The catalytic upgrading could not only eliminate significantly the oxygen of these phenolic compounds but also reduce the amount of tar and heavy components. Pd-Fe catalyst was recognized as a suitable catalyst for upgrading of lignin-derived bio-oil since it produced more deoxygenated products and less gas-phase yield than Pd-Co catalyst.

### 1. Introduction

Bio-oil from biomass pyrolysis is considered a promising secondgeneration biofuel [1]. However, it is very difficult to directly utilize the pyrolysis oil because of its high water and oxygen contents [2,3]. The presence of oxygenated compounds (e.g. acids, esters, alcohols, ketones, furans, phenols) makes the bio-oil low heating value, low thermal stability, high viscosity and corrosiveness [4-6]. Therefore, the upgrading step was required to produce the useful chemical and fuel from bio-oil. There are some upgrading processes such as catalytic cracking, hydrodeoxygenation (HDO), supercritical fluids, esterification, emulsification, molecular distillation, and catalytic pyrolysis [7,8]. Catalytic HDO is a prominent process which not only eliminate the oxygen, but also preserve the carbon number of the bio-oil [9,10]. To date, there have been numerous studies on HDO of model compound and real bio-oil over different types of catalysts, such as transition metal sulfide (CoMoS and NiMoS) [7,11], transition metal phosphide (Ni<sub>2</sub>P and Co<sub>2</sub>P) [4,12,13], noble metals (Ru, Pt and Pd) [3,14-16], and base metals (Cu, Fe, Co and

### Ni) [9,17–19].

Lignocellulosic biomass has been recognized as the most abundant renewable resources to produce biochemical, biofuel and biomaterial [20,21]. Furthermore, the potential amount of lignin is very interesting since the development of ethanol fuel, cellulose rich fiber production and paper industries which use cellulose and leave lignin as a residue [22–24]. Lignin can be utilized as the renewable aromatic resources for petrochemical production [21–23]. Guaiacol (2-methoxyphenol) is the major phenolic compound in the lignin-derived bio-oil, and it is a challenging component for HDO upgrading process [9,22]. Guaiacol is usually chosen as a model compound for HDO study because it contains both major functional groups of lignin-derived phenolic such as hydroxyl (-OH) and methoxy ( $-OCH_3$ ) groups [15]. Numerous researchers studied the HDO of guaiacol since it presents as a strong component which is more difficultly deoxygenated than other phenolic compounds (i.e. anisole and cresol) [14–16].

In catalytic process, the continuous-flow operating is more promising and feasible in scaling up than the batch autoclave study [25]. Table 1

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summarizes the HDO of guaiacol as the model compound in the continuous fixed-bed reactor at ambient or high pressure. Previous studies on HDO of guaiacol in the continuous flow system reveal that high H<sub>2</sub>/feed ratio (i.e. 100-600), W/F ratio and reaction temperature (i.e. 450  $^{\circ}$ C) were required to completely remove the oxygen [9,13]. When applied the low H<sub>2</sub>/guaiacol ratio (i.e. 10), the HDO of guaiacol could not produce any oxygen-free aromatic products [26]. In addition, high-pressure reactions (30-69 bar) produced more ring saturation products than ambient pressure [27]. In high-pressure fixed-bed reactor, guaiacol were diluted with organic solvents (i.e. toluene, n-hexadecane or *n*-tridecane) as the feedstock [11,14,28]. This dilution step attributed to the cost of the process and limited the reaction temperature due to the low thermal stability of solvents.

Upgrading of actual bio-oil is a great challenge since the thermal repolymerization reactions usually occur before HDO, forming the solid lignin oligomers [12,29,30]. Hence, most of research works in upgrading of real bio-oil have been done with the batch autoclave reactor instead of the continuous flow reactor [31–34]. There is very few studies in upgrading of bio-oil using the continuous flow reactor [3,4,7,35]. In Wang's study, 10 wt% bio-oil in 1-methylnaphthalene was upgraded over a sulfided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the fixed-bed reactor operating at 96 bar and 330 °C [7]. They found that the carboxyl group was mostly removed by decarboxylation or decarbonylation, while the methoxyl and hydroxyl groups were eliminated by HDO. However, this study did not give the detail of products yield or HDO yield to clarify the effect of polymerization and gasification on bio-oil upgrading process. Sanna et al. [3] studied the hydrogenation and HDO of the aqueous fraction of bio-oil in a two stages continuous reactor with Ru/C and Pt/C catalysts. The reaction temperatures were set at 125 and 275 °C for first and second reactor, respectively, while the operated pressure was kept at 100 bar for both reactors. This 2-stage process could convert 45 % carbon of the aqueous fraction of bio-oil to gasoline blend-stocks and C2 to C6 diols. Recently, Koike et al. [4] conducted fast pyrolysis and catalytic upgrading successively at ambient atmosphere. The system included a fluidized bed pyrolyzer and a fluidized bed catalytic reactor. The  $Ni_2P/SiO_2$  catalyst could reduce moderately the oxygen content of bio-oil (ca. 40 %). They proposed some reactions occurred during catalytic upgrading process such as hydrodeoxygenation, hydrogenation, decarbonylation, and hydrolysis. The refined bio-oil mainly contained phenolic compounds with no carbonyl or methoxy groups.

In this study, the HDO of lignin-derived phenolic components over Al-MCM-41 supported Pd-Co and Pd-Fe catalysts were investigated in a fixed-bed reactor at ambient pressure. The Al-MCM-41 is an acidic and mesoporous support which can enhance the transalkylation activity and stability of catalyst in HDO process [36-39]. Initially, the HDO of guaiacol was conducted to screen the activity and stability of the catalysts. Moreover, the upgrading of actual lignin-derived bio-oil was investigated with bimetallic Pd-Co and Pd-Fe/Al-MCM-41 catalysts in the two-stage catalytic pyrolysis reactor.

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### 2. Experimental

### 2.1. Catalyst preparation and characterization

Aluminosilicate Al-MCM-41 support (3-4 mol% Al<sub>2</sub>O<sub>3</sub>) supplied by ACS Material was activated in air at 500 °C for 14 h. The bimetallic catalysts containing 10 wt% Co or Fe metal and 2 wt% Pd metal were prepared by an incipient wetness co-impregnation method. The support was impregnated with aqueous solutions containing metal precursors (palladium(II) nitrate, cobalt(II) nitrate (99.999 %) and iron(III) nitrate (99.95 %) purchased from Sigma Aldrich) for 16 h at 33 °C, and then dried at 105 °C for 8 h, followed by calcination at 500 °C for 4 h in air. The calcined catalysts were sieved to give the particles of 35-60 mesh in the size range.

The TriStar II 3020 was used to measure the nitrogen adsorption/ desorption isotherms at -196 °C. The catalyst was pretreated at 300 °C for 4 h in nitrogen gas. Transmission electron microscopy (TEM) image was obtained on a Carl Zeiss LIBRA® 200FE (operating voltage 200 kV). The catalyst powder was dispersed ultrasonically in 2propanol for 15 min and then deposited on a carbon coated copper grid for TEM measurement. The catalyst was also characterized with the scanning transmission electron microscopic (STEM) images by a JEM-ARM200F (JEOL) instrument at an accelerating voltage of 200 kV. The STEM provides 3 types of images i.e. SE (secondary electron image), ZC (Z contrast image) and TE (transmission electron image). The SE image provides information for the exterior surface of the carrier, while the ZC and TE images provide information for both interior and exterior surface of the carrier.

Temperature programmed reduction (TPR) in hydrogen was carried out using a Thermo Scientific TPDRO 1100 instrument. Samples were pretreated in nitrogen at 120 °C for 60 min. Then, a TPR program was performed with a heating rate of 10 °C/min from room temperature to 900 °C hold for 30 min under 5 %  $H_2/N_2$  flow. The amount of hydrogen consumption during catalyst reduction process was monitored by a thermal conductivity detector (TCD). The acidity of Al-MCM-41 was determined by temperature programmed desorption (TPD) of ammonia (using Micromeritics AutoChem II 2920). Initially, the sample ( $\sim 0.03$  g) was degassed at 200 °C at heating rate of 10 °C/min for 1 h under constant helium flow (30 mL/min). Then, sample was cooled to 115 °C and 10 % NH<sub>3</sub>/He was adsorbed for 30 min. After saturation, helium was purged for 15 min at 30 mL/min to remove excess ammonia on the catalyst surface. Finally, the sample was heated from 115 to 900 °C under constant helium flow (30 mL/min). The concentration of desorbed ammonia was quantified by a TCD.

Thermogravimetric analysis (TGA) under the flow of air was conducted in a TA Instrument model QA50. During the analysis, temperature was increased from room temperature to 900 °C at a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) pattern was performed on a PANalytical Expert<sup>3</sup> X-ray diffractometer using Cu Kα radiation. XRD

Table 1

Literature studied on HDO of guaiacol in continuous flow rea	ctor.
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Literature stu	idied on HDO of	f guaiacol in conti	inuous f	flow re	actor.							
Year/Ref.	Reactant	Catalyst	Т	Р	W/F	H <sub>2</sub> /Gua	X <sub>Gua</sub>		Product Yield*/Selectivity (%)			
			°C	bar	h		%	Cyclo-alkane	Aromatic	Mono-oxygenated	Di-oxygenated	Gas phase
2011 [ <mark>12</mark> ]	Guaiacol	Ni <sub>2</sub> P/SiO <sub>2</sub>	300	1	0.71	33	80	0	60	40	0	NA
2013 [9]	Guaiacol	Pd-Fe/C	450	1	0.75	100	98	0*	87*	0*	0*	11*
2013 [ <mark>13</mark> ]	Guaiacol	Ni <sub>2</sub> P/SiO <sub>2</sub>	300	1	1.5	600	99.5	0*	71.9*	2*	0*	5.7*
2013 [17]	Guaiacol	Fe/SiO <sub>2</sub>	400	1	7.5	50	100	0*	75*	8*	0*	17*
2014 [26]	Guaiacol	Pt/C	300	1	0.3	10	88	0	0	70	8	22
2016 [40]	Guaiacol	Co/Al-MCM-41	400	1	1.67	25	99.5	0	34.4	25.5	0.9	29.7
2016 [ <mark>18</mark> ]	Guaiacol	Fe/Ni/Hbeta	400	1	4.0	40	100	5.59*	6.11*	86.5*	0*	1.79*
2016 [41]	Guaiacol	Ni@Pd SD	450	1	2.4	25	83	0	52	35	0	NA
2012 [14]	3.0 wt.% gua	Pt/MZ-5	200	40	0.5	110	100	92	0	0	0	NA
2014 [28]	0.4 mol% gua	Pt/MgO	250	69	3.74	17	62.9	25	0	63.6	1.6	10
2016 [11]	3.0 wt.% gua	CoMoS/CCA	260	30	0.42	500	92	11	31.5	47.3	2.2	NA
2017 [27]	Guaiacol	Ni-Fe/CNT	300	30	0.17	50	96.8	83.4	3.2	12.7	0.7	NA

\* Indicate the product yield.

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pattern was recorded at speed of  $2^{\circ}$ /min with step-sizes of  $0.02^{\circ}$  in the diffraction angle range of  $2-70^{\circ}$ .

### 2.2. HDO of guaiacol

Catalytic HDO reaction was conducted in a fixed-bed tubular reactor (internal diameter of 13 mm) made of stainless steel at 400 °C and ambient pressure. The detail of the experimental set-up of HDO of guaiacol was mentioned elsewhere [42] (see Fig. S1). Before HDO reaction, all catalysts were reduced at 450 °C using a hydrogen flow of 90 mL/min for 2 h. Pure guaiacol was fed at a flow rate of 1.08 mL/h using a syringe pump and vaporized at 350 °C in the top glass wool bed. In HDO of guaiacol experiments, the carbon balance was between 93 and 98 % except the HDO over Pd catalyst (88 %). The liquid products were quantified by gas chromatography (Shimadzu GC-2014), with a SGE BPX-5 capillary column (30 m, ID 0.25 mm, 0.25 µm) and a flame ionized detector (FID). Sample was diluted in acetone, and n-dodecane was used as an internal standard (ISTD) for all analysis. The non-condensed gas was analyzed with GC-TCD system (Shimadzu GC-8A) which consisted of two columns, i.e. porapak Q (for CO<sub>2</sub> and  $CH_4$  analysis) and molecular sieve 5A (for  $H_2,\,N_2,\,O_2,\,CH_4$  and CO analysis). Carbon-based guaiacol conversion ( $X_{Gua}$ ), product yield ( $Y_i$ ) and HDO yield were calculated in Mol<sub>Carbon</sub>% by the following equations.

$$X_{Gua} (\%) = \frac{Mol(gua)_{in} - Mol(gua)_{out}}{Mol(gua)_{in}} \times 100$$
<sup>(1)</sup>

$$Y_i (\%) = \frac{Mol_i \times \alpha_i}{Mol(gua)_{in} \times 7} \times 100$$
<sup>(2)</sup>

HDO yield (%) = 
$$\sum \frac{Y_i \times (2 - \beta_i)}{2}$$
 (3)

where  $\alpha_i$  and  $\beta_i$  are the carbon and oxygen numbers in product *i*.

### 2.3. Catalytic upgrading of lignin-derived bio-oil

Alkali lignin powder (purchased from Sigma Aldrich) was used as biomass reactant for pyrolysis and catalytic upgrading processes. The lignin feedstock has a water content of 7.5 wt%, and the elemental composition (wt%, dry basis): 66.5 % C, 7.1 % H, 0.8 % N, and 2.0 % S. The tubular fixed-bed reactor was used for both pyrolysis and catalytic upgrading processes (see Fig. S1). Lignin (3.0 g) was packed in the top part of reactor and sandwiched with glass wool. Meanwhile, the bottom part of reactor was packed with glass wool only in the pyrolysis process (without catalyst). Catalyst was added to the bottom part in the upgrading process with amount of 1.5 g (catalytic upgrading). The reactor outlet line was heated at  $\sim 195~^\circ\text{C}$  to avoid the condensation of liquid products before they reached the 2-stage cold trap. The first cold trap was empty and cooled by ice water ( $\sim 5$  °C), while the second cold trap contained acetone and cooled by ethylene glycol ( $\sim$  -10 °C). The condensed liquid collected at first and second cold traps were named by heavy and light oil, respectively. These liquid products were diluted with acetone and analyzed with GC-FID and Karl Fisher (KF). Meanwhile, the non-condensed gas was sampled every 15 min, and analyzed with GC-TCD. After reaction, the remained char (char residue) at the top part of reactor was collected and weighted. In catalytic upgrading process, the coke deposit on the catalyst was calculated from the mass loss (from 200 to 700 °C) using TGA data.

The pyrolysis of lignin was conducted in hydrogen gas at 500 °C with the heating rate of 80 °C/min. The two-stage catalytic pyrolysis process (catalytic upgrading) was carried on in hydrogen gas at the temperatures of lignin and catalyst bed of 500 and 400 °C, respectively. Hydrogen was used in both pyrolysis and catalytic upgrading experiments in order to clearly clarify the effect of catalyst in the upgrading process. The volatile product of pyrolysis process at the top part was flowed to the catalyst

bed at the bottom part for upgrading process. The experiment was kept for 90 min until no observation of volatile in the cold trap. The products of lignin conversion process might contain bio-char (top part of reactor), coke deposit (catalyst bed), tar (bottom flange and reactor wall), heavy bio-oil (first cold trap), light bio-oil (second cold trap) and bio-gas (noncondensed gas). The product yields were calculated on a dry base yield with the water content of lignin is 7.5 wt%.

$$Y_{water} (\%) = \frac{M_{water} - M_{biomass} \times 0.075}{M_{biomass} \times (1 - 0.075)} \times 100$$
(4)

$$Y_i (\%) = \frac{M_i}{M_{biomass} \times (1 - 0.075)} \times 100$$
(5)

which  $M_i$  is the mass of product *i* and  $M_{biomass}$  is the mass of lignin.

### 3. Results and discussion

## 3.1. Characterization of Al-MCM-41 supported Pd-Co and Pd-Fe catalysts

Table 2 demonstrates the textural properties of Al-MCM-41 supported monometallic and bimetallic catalysts. The metal-modified Al-MCM-41 catalysts showed a decrease in surface area and pore volume as expected. It may be caused by the partial blockage of pores after metal deposition [38]. The higher metal was loaded, the more difference between support and metal-modified catalysts was observed. As shown in Table 2 and Fig. S2, all metal-modified Al-MCM-41 catalysts still maintained same mesoporosity structure. Pore size distribution remained the sharp peak at around 3 nm (Fig. S2). It suggests that the metal deposition only caused the partial blockage of pores instead of destroying the framework structure of Al-MCM-41 support. The total acidity (Brønsted and Lewis acidity) of Al-MCM-41 measured by NH<sub>3</sub>-TPD was 1.06 mmol/g. The acidity of Al-MCM-41 is caused by the Al atoms incorporated in the MCM-41 framework [43,44].

The TEM images of the mono- and bi-metallic catalysts are displayed in Fig. 1, including the size distribution diagrams of metal oxide particles. Although most of the particles were in a size range between 3 and 9 nm, larger particles up to 23 nm were also detected. The monometallic Co and Fe catalysts had broader size distributions of metal oxide particles from 2 to 23 nm while the bimetallic Pd-Co and Pd-Fe catalysts had narrower size distributions from 2 to 16 nm. This observation confirmed the advantage of bimetallic in particle size distribution of metal oxide comparing with monometallic [10,41,42]. To further study of the structure of catalyst, the STEM image was done for the Pd-Fe/Al-MCM-41 sample (Fig. 2). The SE, ZC and TE images show that most of the small particles ( $\sim$  3 nm) existed inside the porous of Al-MCM-41 support.

The temperature-programmed reduction (TPR-H<sub>2</sub>) profiles of Al-

### Table 2

Textural properties of fresh Al-MCM-41 supported mono- and bi- metallic catalysts.

Samples	BET surface area	Pore size <sup>a</sup>	Pore volume <sup>a</sup>	Coke formation <sup>b</sup>
	(m <sup>2</sup> /g)	(nm)	(cm <sup>3</sup> /g)	wt%
Al-MCM-41	742	3.21	0.56	
10Co/Al-MCM-41	583	3.33	0.43	$16.8 \pm 0.9$
10Fe/Al-MCM-41	573	3.74	0.44	$21.7 \pm 0.2$
2Pd/Al-MCM-41	630	3.53	0.49	$15.6 \pm 0.6$
2Pd10Co/Al-	490	3.72	0.39	$12.8\pm0.2$
MCM-41				
2Pd10Fe/Al-	507	3.69	0.42	$17.5\pm0.3$
MCM-41				

<sup>a</sup> Calculated by BJH adsorption theory.

 $^{\rm b}$  Calculated by the mass loss (from 200 to 700  $^{\circ}\text{C})$  of used catalyst in TGA analysis.



Fig. 1. TEM image of fresh catalysts. A) Co/Al-MCM-41, B) Fe/Al-MCM-41, C) Pd-Co/Al-MCM-41, D) Pd-Fe/Al-MCM-41.



Fig. 2. STEM images of fresh Pd-Fe/Al-MCM-41.

MCM-41 supported metal catalysts are displayed in Fig. 3. The reduction profile of Pd catalyst showed a small peak at 170 °C. It has been known that PdO can be reduced readily below ambient temperature [9,45]. This difference indicates the formation of strong interaction of PdO with support in our catalyst [46]. The monometallic Co catalyst had three distinct peaks at around 360, 385 and 690 °C, which were associated with the reduction of Co<sub>3</sub>O<sub>4</sub>, CoO, and exchanged Co<sup>2+</sup> ions, respectively [45–49]. In the other hand, monometallic Fe had three reduction peaks at 445, 580 and 715 °C for the stepwise reductions of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> to FeO, and FeO to Fe metal [50–53]. In general, Co oxides might be reduced more readily than Fe oxides. The addition of Pd to Co and Fe catalysts significantly lowered the reduction temperature. Both bimetallic catalysts had a sharp peak at around 100 °C which is likely the

co-reduction of small Pd-Fe and Pd-Co alloy particles [9,52]. All the peaks appeared in monometallic Co and Fe catalysts are shifted to lower reduction temperature in bimetallic catalyst. These TPR results clearly demonstrated the presence of hydrogen spillover effect where a noble metal acts like the spilling source while a transition metal oxide is the receptor [47,46–49]. The H<sub>2</sub> consumption for each reduction peak was calculated and showed in the Table S1, in which  $Co_3O_4$  and  $Fe_2O_3$  presented as the major oxides in the corresponding fresh catalysts. The TEM and TPR results imply that the addition of Pd could enhance the dispersion and reducibility of Co and Fe oxides.

Fig. 4.A and B illustrate the powder XRD patterns of the fresh and reduced Al-MCM-41 supported metallic catalysts, respectively. The metal-modified catalysts have a broad peak at around 23° which is



Fig. 3. Hydrogen temperature-programmed reduction (TPR-H $_2$ ) of fresh catalysts.

assigned to an amorphous silica in Al-MCM-41 support [54]. The fresh Co-modified catalyst had five diffraction peaks at 31.3°, 36.8°, 44.9°, 59.3°, and 65.2° corresponding to different Co<sub>3</sub>O<sub>4</sub> crystallites [53,55, 56]. Meanwhile, there are 7 peaks of Fe<sub>2</sub>O<sub>3</sub> in the XRD pattern of fresh Fe catalyst [52,53,57]. The fresh bimetallic catalysts had similar XRD patterns comparing to the monometallic ones with the addition of PdO peak at 33.8° [44,46,47]. The addition of Pd did not significantly change the crystallographic characteristics of Fe and Co catalysts [47,57]. After reduction, the broad peak of amorphous silica was remained as displayed in Fig. 4B. The reduced Co catalyst had a low intensity peak of CoO at  $42.3^{\circ}$  besides the main peak of metallic Co at  $44.6^{\circ}$  [46,58–61]. The present of CoO peak in reduced sample might be from either re-oxidation when the catalyst was exposed to air during the storage period [58,60,61] or incompletely reduction at chosen condition. The reduced Fe catalyst remained the peaks of Fe<sub>2</sub>O<sub>3</sub> spinel, implying that Fe<sub>2</sub>O<sub>3</sub> was more difficult to reduce than others. This phenomenon is in agreement with the TPR-H<sub>2</sub> results in Fig. 3. In the bimetallic Pd-Co and Pd-Fe catalysts, Co and Fe oxides were completely reduced, resulting in the formation of Co° (at 44.6°) [46,61] and Fe° (at 44.6° and 65.0°) [17, 57,62]. The XRD results confirmed that Pd could promote the reduction of Co and Fe. According to literatures, XRD pattern of reduced mono Pd catalyst had two distinct peaks at 40.7° and 46.0° [41,62-64]. The shifting of these diffraction peaks to the higher angle in two Pd-Co and

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Pd-Fe catalysts (Fig. 4B) implied that Pd could be formed in Pd-Co and Pd-Fe alloys [62,65].

### 3.2. Hydrodeoxygenation of guaiacol

### 3.2.1. The synergistic effect of bimetallic in catalytic HDO

Fig. 5 compares the conversion of guaiacol and product yields over the supported mono- and bi-metallic catalysts at the same conditions. Monometallic Fe catalyst showed higher HDO and lower gasification activities than monometallic Co due to its higher mono-oxygenated products and lower gas phase (which mainly contained methane) yield. Meanwhile, Pd was found as a poor catalyst for HDO of guaiacol since it produced catechol and other dioxygenated products as the major products. These heavy and viscous products might remain in the reactor wall, caused the lowest carbon recovery of Pd catalyst (around 88 %). Addition of Pd to Co catalyst not only increased the conversion and deoxygenated product yields (aromatics and monooxygenated) but also decreased the gas phase yield. However, this addition to Fe catalyst only showed the increase of mono-oxygenated products, following by the decrease of oxygen-free aromatic yield. In previous paper, we found that HDO of guaiacol occurred via CAr-OCH3 cleavage then CAr-OH cleavage to obtain oxygen-free aromatic as the final product [40]. The combination of Pd and Fe might not favor the CAr-OH cleavage reaction, resulting in a slight decrease of oxygen-free aromatic yield of Pd-Fe catalyst.

Fig. 6 demonstrates the variations of guaiacol conversion and HDO vield with time on stream (TOS). The monometallic Co and Fe catalysts showed faster deactivation than others. Although Pd catalyst had the lowest HDO yield, this catalyst appeared very high stability during the reaction. Therefore, the addition of Pd enhanced significantly the stability of both Co and Fe catalysts. Among all five catalysts, Pd-Fe showed the highest stability and HDO yield. The highest HDO yield of Pd-Fe was attributed by low gas-phase yield and high monooxygenated products yield. In addition, Fig. 7 compares the conversion and product distribution of bimetallic Pd-Co and Pd-Fe catalysts at higher W/F ratio of 1.67 h. As the W/F ratio were increased, the guaiacol conversion and deoxygenated products yield were also increased. Although Pd-Co catalyst showed higher oxygen free product yield, the methane yields was much higher than Pd-Fe catalyst, resulting in lower HDO yield. The Pd-Fe catalyst had higher ratio of phenol to methylated-phenol (C7-10 monooxygenated) than Pd-Co catalyst due to the methyl group was produced less. In general, the hydrogenolysis of CAr-OR and multiple C-C bindings occurred simultaneously in the catalytic HDO over Pd-Co or Co catalysts, resulting in low HDO yield. Meanwhile, Pd-Fe and Fe



Fig. 4. XRD patterns of Al-MCM-41 supported Pd-Co and Pd-Fe catalysts. A) Fresh catalyst and B) Reduced catalysts.



Fig. 5. HDO of guaiacol over mono and bimetallic catalysts. Reaction conditions: T = 400 °C, P =1 bar, W/F =0.83 h, H<sub>2</sub>/Gua = 25, TOS = 30 min.



Fig. 6. Guaiacol conversion and HDO yield of HDO reactions over mono- and bi-metallic catalysts. Reaction conditions: T = 400 °C, P = 1 bar, W/F = 0.83 h,  $H_2/Gua = 25$ .



Fig. 7. Guaiacol conversion and products yield of HDO reactions over bimetallic catalysts. A) Pd-Co, B) Pd-Fe. Reaction conditions: T = 400 °C, P = 1 bar, W/F = 1.67 h,  $H_2/Gua = 25$ .

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favored the  $C_{Ar}$ -OCH<sub>3</sub> hydrogenolysis and inhibited the successive C—C hydrogenolysis, yielding higher HDO yield.

To understand the contribution of Pd to the stability of Co and Fe catalysts, the TGA of used catalysts was applied to understand the coke formation in catalysts as shown in Fig. S3. The main peaks in DTG curves were observed from 200 to 700 °C which associated with coke removal by oxidation. As shown in Table 2, the bimetallic Pd-Co and Pd-Fe catalysts have lower coke formation than the corresponding monometallic catalysts. The addition of Pd reduced the coke formation during HDO reactions and made the catalyst more stable. Additionally, the used Fe and Pd-Fe catalysts had higher coke deposit than the used Co and Pd-Co catalysts. Nevertheless, the stability of the Fe and Pd-Fe catalysts was higher than that of the Co and Pd-Co catalysts (see Fig. 6). This contradiction could be explained by the DTG results (Fig. S3), in which the used Fe and Pd-Fe catalysts had lower temperature degradation peaks (at 350 °C) than Co and Pd-Co catalysts (at 500 °C). Therefore, the coke deposit during catalytic HDO over Fe and Pd-Fe catalysts was more easily degraded than the one over Co and Pd-Co catalysts.

### 3.2.2. Reaction network

HDO experiments were conducted over Pd-Co and Pd-Fe catalysts by varying the W/F ratio for reaction network study (detail can be found in our prior work [66]). Based on the detail analysis of species in the product stream, the possible pathways were proposed as seen in Scheme network comprised HDO, 1. This reaction decarbonylation/decarboxylation, demethylation, cracking, and methyl transfer. The kinetic results were summarized in Table S2. In the case of Pd-Co, the demethylation of guaiacol to form catechol is the major pathway while the formation of phenol through demethoxylation of guaiacol is very slow (k"10 > > k"1, Table S2). The formation of phenol through demethylation of catechol is very fast, it explained the low concentration of catechol in the products. The formation of anisole is the slowest reaction among three intermediates and following the rule of bond dissociation energy (BDE) which ranked as  $C_{Ar}O-CH_3 < C_{Ar}-OCH_3 <$ CAr-OH [67]. In contrast, the formation of phenol from guaiacol is higher than that of catechol in Pd-Fe catalyst (k"1 > > k"10, Table S2). It suggests that phenol was directly formed through demethoxylation of guaiacol rather than from catechol in the present of Pd-Fe catalyst, and the similar results were also observed in the literatures [9,68,69]. This hypothesis was further confirmed by the presence of methanol in HDO

products of guaiacol over Pd-Fe catalyst, but no methanol was observed in that over Pd-Co catalyst. In summary, the major reaction pathway of guaiacol is as following: guaiacol  $\rightarrow$  catechol  $\rightarrow$  phenol  $\rightarrow$  benzene for Pd-Co catalyst, and guaiacol  $\rightarrow$  phenol  $\rightarrow$  benzene for Pd-Fe catalyst. Besides the metallic sites, support also plays an important role in the reaction network. The presence of acid sites in Al-MCM-41 catalyzed the transalkylation of the methyl groups (blue arrows in Scheme 1) which help to minimize the carbon loss via methanization. The combination of HDO by metal sites and transalkylation by acid sites could produce the C<sub>6-12</sub> aromatics (from benzene to hexamethylbenzene) in the products.

### 3.3. Catalytic upgrading of lignin-derived bio-oil

The upgrading of lignin-derived bio-oil was conducted in the twostage catalytic pyrolysis reactor at ambient pressure. The products consisted of char residue, coke deposit, tar, heavy and light oils, and gas phase, and their yields were compared in Fig. 8A and B. In our experiment, the yield of tar and others was estimated by difference. This dark brown tar-like material was observed at the wall and the bottom flange of the stainless-steel reactor. As shown in Fig. 8A, the bio-char yields of all experiments had no significant difference since the bio-char was only produced from pyrolysis process at the top part of reactor. The percentage of biochar after pyrolysis is consistent with the mass loss of lignin which recorded from TGA analysis in nitrogen atmosphere (Fig. S4). The amount of fixed-carbon in lignin is high [70], hence the yield of bio-char from lignin pyrolysis was significant. Comparing with the pyrolysis of cedar chips in Koike et al. research [4], the pyrolysis of lignin in this study had higher bio-char and lower gas-phase yields. The hemicellulose and cellulose in cedar chips in their study could be more easily degraded to form the light component in the gas phase than lignin in this reserach. In catalytic upgrading process, the coke deposit on the Pd-Fe catalyst was higher than that on the Pd-Co catalyst. This trend is similar to the coke deposit during HDO of guaiacol as in Table 2. Additionally, the dark brown tar yield in pyrolysis experiment was obtained more significantly than in catalytic upgrading process. The acid sites of Al-MCM-41 support might catalyzed the cracking reaction of the heavy compounds, resulting in the decrease of tar yield. The gas product, consisted of CH<sub>4</sub>, CO and CO<sub>2</sub>, was produced more significantly in catalytic upgrading than without catalyst.



The liquid products were mostly collected at first cold trap and

Scheme 1. Possible reaction pathways for HDO of guaiacol over Pd-Fe and Pd-Co catalysts.



**Fig. 8.** Upgrading of lignin-derived bio-oil over Pd-Fe and Pd-Co catalysts, A) Product yields, B) Liquid-phase (light and heavy oil) yields. Pyrolysis condition: T = 500 °C, m<sub>Lignin</sub> = 3.0 g. Upgrading condition: T = 400 °C, P =1 bar, m<sub>Cat</sub> = 1.5 g, H<sub>2</sub> flow rate = 90 mL/min.

considered as heavy oil, while the light oil was collected in a relatively small amount (less than 0.9 wt% yield). The visual image of three heavy oil samples is shown at the top of Fig. 9A. The oil was separated to three layers, i.e. heavy-organic phase, aqueous phase and light-organic phase. The heavy oil obtained via catalytic upgrading had less heavy-organic phase and more light-organic phase than that via without catalyst. It implied that the catalyst could catalyze not only deoxygenation reaction but also cracking reaction of the heavy compounds, yielding more lightorganic phase. These reactions attributed to the decrease of heavy oil and tar yields in catalytic upgrading process comparing to the pyrolysis process (Fig. 8A). Comparing to without catalyst, the catalytic upgrading had lower methanol, dioxygenated and trioxygenated phenolics yield and higher water yield (Fig. 8B). The catalytic HDO helped remove the oxygen in methanol, di- and tri-oxygenated phenolics to produce the deoxygenated products and water, resulting in higher water yield of the catalytic upgrading. In addition, the liquid-phase product of the Pd-Co contained more water, dioxygenated and less monooxygenated compounds than the Pd-Fe as shown in Fig. 8B. Similar to HDO of guaiacol discussion, the Pd-Co catalyzed simultaneously the multiple C-C, CAr- $O{-}CH_3$  and  $C_{Ar}{-}OH$  hydrogenolysis while the Pd-Fe showed as an effective catalyst in CAr-OCH3 hydrogenolysis. Hence, the Pd-Co upgrading of lignin-derived bio-oil produced not only more gas phase and dioxygenated compounds but also less monooxygenated than the Pd-Fe upgrading.

Fig. 9A and B show the GC-FID chromatography of heavy and light oil products. The lignin-derived bio-oil of without catalyst had much more dioxygenated and trioxygenated phenolic compounds i.e. guaiacol (7), methyl-guaiacol (9), catechol (10) and dimethoxy-phenol (12) than that of catalytic upgrading samples. These products were further deoxygenated in catalytic upgrading process to produce the monooxygenated and oxygen-free products. The oxygen-free aromatic products, which contained benzene and toluene as the major compound, were mostly collected at the second cold trap (Fig. 9B). Toluene, which formed by HDO and transalkylation reactions, was found as the major aromatic in bio-oil product. Some heavier components (Other products) could not be determined with our GC-FID analysis and appeared more in without catalyst sample. Moreover, the Pd-Fe catalyst showed higher HDO activity and lower gasification activity than the Pd-Co catalyst, yielding higher signal intensity of mono-oxygenated peaks (Fig. 9A).

Zhang et al. studied the HDO of lignin-derived bio-oil over Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> at 300 °C and 50 bar for 8 h in an autoclave reactor [22]. Their feedstock was prepared separately by degradation of lignin in a stirred autoclave at 280 °C for 1 h with the present of 5 wt.% ZnCl<sub>2</sub> and methanol. The major component in their lignin-derived bio-oil were guaiacol, xylenol, trimethylphenol, propylanisole and cresol which were similar with our results. However, their high-pressure process produced more cyclic saturated hydrocarbons (yield of 55.0 wt%) than aromatic hydrocarbons (yield of 7.8 wt%) in the upgraded products. Our experiments were conducted at atmospheric pressure hence no saturation product was observed.

The lignin-derived pyrolysis oil mainly contained phenolic compounds which had one to three oxygen atoms. The catalytic upgrading can eliminate significantly the oxygen in phenolic molecules to produce the lower oxygen content pyrolysis oil. In addition, the increase of water (liquid phase) and  $CO + CO_2$  (gas phase) in catalytic upgrading indicated that the oxygen could be eliminated by both HDO and decarboxvlation/decarbonylation [4,7]. In general, the HDO was catalyzed by metallic sites while the decarboxylation/decarbonylation was catalyzed by acid sites of Al-MCM-41 support. The Pd-Co catalyzed the multiple C-C, CArO-CH3 and CAr-OH hydrogenolysis. These reactions helped to reduce the oxygen and tar content but raise the carbon loss to the gas phase. The Pd-Fe favored the CAr-OCH3 hydrogenolysis and some cracking reaction which could reduce the oxygen and tar yield and preserve the carbon in the bio-oil. In summary, Pd-Fe presented better performance since it produced not only more mono-oxygenated phenolic but also less dioxygenated, trioxygenated and gas-phase products than Pd-Co catalyst.

### 4. Conclusion

Hydrodeoxygenation of guaiacol and lignin-derived bio-oil over Al-MCM-41 supported Pd-Co and Pd-Fe catalysts have been studied at 400 °C and 1 atm. The Fe catalyst gave higher HDO yield and lower gas phase yield compared with the Co catalyst in HDO of guaiacol. The bimetallic Pd-Co catalyst presented a higher HDO activity than the monometallic Co while the Pd-Fe showed an insignificant improvement in HDO activity. Interestingly, the addition of Pd significantly improved the stability of catalysts since it could reduce the coke deposition on the catalysts.

The upgrading of actual lignin-derived bio-oil was conducted successfully in a fi xed-bed reactor. The Pd-Co and Pd-Fe catalysts could eliminate significantly the oxygen content in lignin-derived bio-oil. The Pd-Co and Pd-Fe catalyzed not only deoxygenation reaction to reduce the oxygen content but also cracking reaction to reduce the tar yield. In catalytic upgrading process, oxygen was removed by both HDO and decarboxylation/decarbonylation. Pd-Co catalyzed simultaneously the C<sub>Ar</sub>O–CH<sub>3</sub>, C<sub>Ar</sub>–OH and multiple C–C hydrogenolysis while Pd-Fe catalyzed principally the C<sub>Ar</sub>–OCH<sub>3</sub> hydrogenolysis. In summary, the Pd-Fe/Al-MCM-41 presented as a suitable catalyst for upgrading of lignin-derived bio-oil since its higher deoxygenated products and lower gas-phase yields than Pd-Co/Al-MCM-41.

### CRediT authorship contribution statement

Nga T.T. Tran: Conceptualization, Investigation, Validation, Writing - original draft, Visualization. Yoshimitsu Uemura: Resources, Project administration, Funding acquisition, Supervision, Writing - review & editing. Anita Ramli: Methodology, Supervision, Writing - review & editing. Thanh H. Trinh: Software, Methodology, Writing - review & editing.

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Fig. 9. Chromatography of heavy oil (A) and light oil (B) products in upgrading of lignin-derived bio-oil on Al-MCM-41 supported Pd-Fe and Pd-Co catalysts.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111435.

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