



# Supplementary material: Catalytic hydro-deoxygenation of acetic acid, 4-ethylguaiaicol, and furfural from bio-oil over Ni<sub>2</sub>P/HZSM-5 catalysts

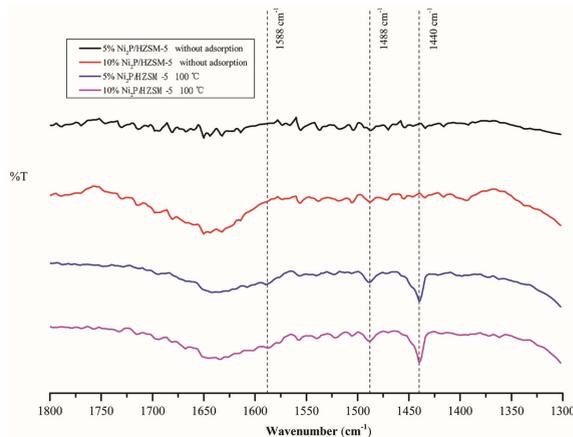
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## 1. Pyridine Fourier Transform Infrared Spectroscopy (FT-IR) characterization

Generally, the acid sites of catalysts include Brønsted and Lewis acid sites. For Ni<sub>2</sub>P-based catalysts, the Brønsted acid sites could be attributed to the surface PO-H groups, and Lewis acid sites are the Ni species with a partial positive charge (Ni<sup>δ+</sup>) [1]. In Figure 3, the bands that appeared at 1440 and 1588 cm<sup>-1</sup> were assigned to pyridine adsorbed on the Lewis acid sites, whereas the presence of band at 1488 cm<sup>-1</sup> was attributed to pyridine adsorbed on both the Lewis and Brønsted acid sites based on the literature [2,3]. Besides, IR spectra of 5% Ni<sub>2</sub>P/HZSM-5 catalysts show a similar acidity compared to 10% Ni<sub>2</sub>P/HZSM-5. Besides, the intensity of the bands on both 5% and 10% Ni<sub>2</sub>P/HZSM-5 catalysts reduced with an increase of the desorption temperature from 100 to 400 °C and was weak at 150, 275, and 400 °C desorption temperature.

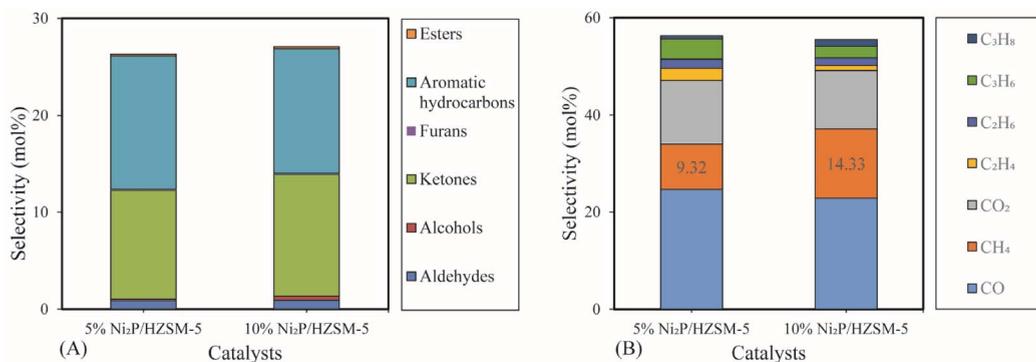


**Supplementary Figure S1.** IR spectra of Ni<sub>2</sub>P/HZSM-5 catalysts at 100 °C desorption temperature (with/without adsorption of pyridine).

## 2. Effect of catalysts on acetic acid HDO

As shown in Table S1, the conversion rate and DOD reached around 81% and 77%, respectively. Clearly, results showed that these catalysts were effective in

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**Supplementary Figure S2.** Effects of catalysts on acetic acid HDO (400 °C, 0.5 MPa, 0.05 mL/min acetic acid, 40 mL/min H<sub>2</sub>, 10 mL/min N<sub>2</sub>, reaction time: 90 min): (A) Selectivity of chemical composition in liquid phase; (B) Selectivity of chemicals in gas phase.

**Supplementary Table S1.** Comparison of different catalysts in acetic acid HDO

Item	Conditions <sup>a</sup>	
	5% Ni <sub>2</sub> P/HZSM-5	10% Ni <sub>2</sub> P/HZSM-5
Conversion rate & DOD (wt%)		
$X_{\text{acetic acid}}$	80	81
$DOD$	77.0	76.1
Yield of products (wt%)		
$Y_{\text{Liq. (free water)}}$	33.09	32.87
$Y_{\text{Gas}}$	41.02	39.66
$Y_{\text{H}_2\text{O}}$	25.89	27.46

<sup>a</sup> Fixed conditions: 0.43 g 5% Ni<sub>2</sub>P/HZSM-5; 0.47 g 10% Ni<sub>2</sub>P/HZSM-5; 400 °C, 0.5 MPa, 0.05 ml/min of acetic acid, H<sub>2</sub>: 40 ml/min, N<sub>2</sub>: 10 ml/min, 90 min.

catalyzing the HDO reaction.

The effect of the 5% and 10% Ni<sub>2</sub>P/HZSM-5 catalysts on the selectivity for the chemical composition in liquid products of acetic acid HDO is compared in Figure S2A. Ketones and aromatic hydrocarbons were the primary products using 5% Ni<sub>2</sub>P/HZSM-5, with the selectivity of 11.2% and 13.8%. The 10% Ni<sub>2</sub>P/HZSM-5 showed similar values of 12.6% for ketones and 12.9% for aromatic hydrocarbons.

Figure S2B shows the effect of the 5% and 10% Ni<sub>2</sub>P/HZSM-5 catalysts on the selectivity for chemicals of acetic acid HDO in gas products. It can be seen that CO, CO<sub>2</sub> and CH<sub>4</sub> were obtained as the main products of acetic acid HDO on Ni<sub>2</sub>P/HZSM-5 catalysts with the selectivities of 24.7% for CO and of 13.1% for CO<sub>2</sub>. The highest selectivity of CH<sub>4</sub> (14.3%)

was obtained using 10% Ni<sub>2</sub>P/HZSM-5. Probably, the high content of Ni<sub>2</sub>P facilitates the decarboxylation reaction of acetic acid for more CH<sub>4</sub> and CO<sub>2</sub> formation. However, the 10% Ni<sub>2</sub>P/HZSM-5 catalyst showed a slightly lower selectivity of CO<sub>2</sub> than the value from 5% Ni<sub>2</sub>P/HZSM-5. This can be explained by the fact that some of the CO<sub>2</sub> and CO was further reacted with H<sub>2</sub> via the methanation reaction to form CH<sub>4</sub> and H<sub>2</sub>O. Similarly, Zhang *et al.* [4] performed the methanation of CO<sub>2</sub> over Ni/Al<sub>2</sub>O<sub>3</sub> and found that the nickel loading of 27.5% allowed the best activity for CH<sub>4</sub> formation at 400 °C. What's more, a higher yield of H<sub>2</sub>O using 10% Ni<sub>2</sub>P/HZSM-5 than 5% Ni<sub>2</sub>P/HZSM-5 (Table S1) was noted, which also confirms that the methanation reaction of CO<sub>2</sub> took place.

### 3. Chemicals in the liquid phase

**Supplementary Table S2.** Main chemicals in the liquid phase of acetic acid HDO

Classification	Chemicals <sup>a</sup>	Formula	O (wt%)
Aldehydes	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	36.4
Alcohols	1-Phenyl-1,2-butanediol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	19.3
Carboxylic acids	Acetic acid <sup>b</sup>	CH <sub>3</sub> COOH	53.3
Esters	2-Naphthalenol, 1,2-dihydro-, acetate	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	17.0
Ketones	Acetone	C <sub>3</sub> H <sub>6</sub> O	27.6
	Methyl isobutyl ketone	C <sub>6</sub> H <sub>12</sub> O	16.0
Aromatic hydrocarbons	Benzene		
	Toluene	C <sub>6</sub> H <sub>6</sub>	
	Ethylbenzene	C <sub>7</sub> H <sub>8</sub>	
	P-xylene	C <sub>8</sub> H <sub>10</sub>	
	O-xylene	C <sub>8</sub> H <sub>10</sub>	
	PropylBenzene	C <sub>8</sub> H <sub>10</sub>	
	Isopropylbenzene	C <sub>9</sub> H <sub>12</sub>	
	1-Ethyl-2-methylbenzene	C <sub>9</sub> H <sub>12</sub>	
	Mesitylene	C <sub>9</sub> H <sub>12</sub>	
	1-Methylindan	C <sub>9</sub> H <sub>12</sub>	
	2,3-Dihydro-4-methyl-1H-indene	C <sub>10</sub> H <sub>12</sub>	
	2,3-dihydro-4,7-dimethyl-1H-Indene	C <sub>11</sub> H <sub>14</sub>	
	2,3-Dihydro-2,2-dimethylindene,	C <sub>11</sub> H <sub>14</sub>	
	1-ethylidene-1H-Indene	C <sub>11</sub> H <sub>14</sub>	
	1,3-Dimethyl-Naphthalene	C <sub>12</sub> H <sub>12</sub>	
p-Cymene	C <sub>10</sub> H <sub>14</sub>		

<sup>a</sup> Only chemicals with content >1 mol% were presented in this table.

<sup>b</sup> Unreacted acetic acid.

**Supplementary Table S3.** Main chemicals in the liquid phase of 4-ethylguaiacol HDO

Classification	Chemicals <sup>a</sup>	Formula	O (wt%)	
Ethers	1-Methoxy-4-(1-methylpropyl)-benzene	C <sub>11</sub> H <sub>16</sub> O	9.8	
	2-Methoxy-4-methyl-1-(1-methylethyl)-benzene	C <sub>11</sub> H <sub>16</sub> O	9.8	
Alcohols	α,β-Dimethyl-benzeneethnol	C <sub>10</sub> H <sub>14</sub> O	10.7	
Ketones	Acetone	C <sub>3</sub> H <sub>6</sub> O	27.6	
	Phenol	C <sub>6</sub> H <sub>6</sub> O	17.0	
Phenols	Cresol (p- & o-)	C <sub>7</sub> H <sub>8</sub> O	25.8	
	3-Ethylphenol	C <sub>8</sub> H <sub>10</sub> O	14.8	
	4-Ethylphenol	C <sub>8</sub> H <sub>10</sub> O	14.8	
	2-Ethylphenol	C <sub>8</sub> H <sub>10</sub> O	14.8	
	2,4-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	14.8	
	3,4-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	14.8	
	2-Ethyl-6-methylphenol	C <sub>9</sub> H <sub>12</sub> O	11.8	
	2-Ethyl-4-methylphenol	C <sub>9</sub> H <sub>12</sub> O	11.8	
	3-Methyl-4-isopropylphenol	C <sub>10</sub> H <sub>14</sub> O	10.7	
	3-Ethyl-5-methylphenol	C <sub>9</sub> H <sub>12</sub> O	11.8	
	3,4,5-Trimethylphenol	C <sub>9</sub> H <sub>12</sub> O	11.8	
	3-5-Diethylphenol	C <sub>10</sub> H <sub>14</sub> O	10.7	
	Thymol	C <sub>10</sub> H <sub>14</sub> O	10.7	
	Guaiacols	2-Methoxyphenol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	25.8
		4-Ethylguaiacol <sup>b</sup>	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	21.1
Alkenes	2,3-Dihydro-1,1,6-trimethyl-1H-Indene	C <sub>12</sub> H <sub>16</sub>		
	9,10-Dihydro-9-(1-methylpropyl)-Anthracene	C <sub>18</sub> H <sub>20</sub>		
	Benzene	C <sub>6</sub> H <sub>6</sub>		
Aromatic hydrocarbons	Toluene	C <sub>7</sub> H <sub>8</sub>		
	P-xylene	C <sub>8</sub> H <sub>10</sub>		
	M-xylene	C <sub>8</sub> H <sub>10</sub>		
	1-Methylethyl-benzene	C <sub>9</sub> H <sub>12</sub>		
	1,9-Dimethyl-9H-Fluorene	C <sub>15</sub> H <sub>14</sub>		
	2-Ethyl-Naphthalene	C <sub>12</sub> H <sub>12</sub>		

<sup>a</sup> Only chemicals with content >1 mol% were presented in this table.

<sup>b</sup> Unreacted 4-ethylguaiacol.

**Supplementary Table S4.** Main chemicals in the liquid phase of furfural HDO

Classification	Chemicals <sup>a</sup>	Formula	O (wt%)
Aldehydes	Butanal	C <sub>4</sub> H <sub>8</sub> O	22.2
	Furfural <sup>b</sup>	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	33.3
Ketones	Acetone	C <sub>3</sub> H <sub>6</sub> O	27.6
	Furan	C <sub>4</sub> H <sub>4</sub> O	23.5
Furans	2-Methylfuran	C <sub>5</sub> H <sub>6</sub> O	19.5
	3-Methylfuran	C <sub>5</sub> H <sub>6</sub> O	19.5
	2,5-Dimethylfuran	C <sub>6</sub> H <sub>8</sub> O	16.7
	2-Vinylfuran	C <sub>6</sub> H <sub>6</sub> O	17.0
	2,2'-Methylenebis-furan	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	21.6
Aromatic hydrocarbons	Benzene	C <sub>6</sub> H <sub>6</sub>	
	Toluene	C <sub>7</sub> H <sub>8</sub>	
	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	
	P-xylene	C <sub>8</sub> H <sub>10</sub>	
	1-Methylethyl-benzene	C <sub>9</sub> H <sub>12</sub>	
	1-Ethyl-3-methylbenzene	C <sub>9</sub> H <sub>12</sub>	
	Mesitylene	C <sub>9</sub> H <sub>12</sub>	
1-Methylindan	C <sub>10</sub> H <sub>12</sub>		

<sup>a</sup> Only chemicals with content >1 mol% were presented in this table.

<sup>b</sup> Unreacted furfural.

## References

- [1] Y.-K. Lee, S. T. Oyama, *J. Catal.*, 2006, **239**, 376-389.
- [2] S. Gutiérrez-Rubio, A. Berenguer, J. Přeč, M. Opanasenko, C. Ochoa-Hernández, P. Pizarro, J. Čejka, D. P. Serrano, J. M. Coronado, I. Moreno, *Catal. Today*, 2020, **345**, 48-58.
- [3] K. Tanabe, <https://agris.fao.org/agris-search/search.do?recordID=US201300474397>.
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