Supporting Information

Ga-doped Cu/H-nanozeolite-Y catalyst for selective hydrogenation/hydredeoxygenation of lignin-derived chemicals

Deepak Verma, a,b,d Rizki Insyani, a Handi Setiadi Cahyadi, a Jae-Yong Park, b Seung Min Kim, c
Jae Min Chao, d Jang Wook Bae, d Jaehoon Kim*, a,b,d

a SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University,
2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, Republic of Korea
b School of Mechanical Engineering, Sungkyunkwan University,
2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, Republic of Korea
c Institute of Advanced Composite Materials, Korea Institute of Science and Technology
Chudong-ro 92, Bongdong-eup, Wanju-gun, Jeonranbuk-do, Republic of Korea
d School of Chemical Engineering, Sungkyunkwan University,
2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, Republic of Korea
Fig. S1 Example of some commercial drugs derived from indane and indanone.¹
Table S1. Summary of the reported HDO reactions of vanillin, acetovanillone, and cinnamaldehyde over various types of heterogeneous catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Feed</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>$P_{\text{H}_2}$ (MPa)</th>
<th>$T$ (°C)</th>
<th>$t$ (h)</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillin</td>
<td>Au/CNTs</td>
<td>H$_2$O$^a$</td>
<td>1.0</td>
<td>200</td>
<td>6</td>
<td>100</td>
<td>75 (Creosol)</td>
<td>75 (Creosol)</td>
<td>Yang et al. RSC Adv. 2014, 4, 31932.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Ru/CNTs</td>
<td>H$_2$O$^a$</td>
<td>1.0</td>
<td>150</td>
<td>3</td>
<td>100</td>
<td>96 (Creosol)</td>
<td>96 (Creosol)</td>
<td>Yang et al. Catal. Comm. 2014, 47, 28.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/CM180$^b$</td>
<td>H$_2$O$^a$</td>
<td>1.0</td>
<td>100</td>
<td>1</td>
<td>&gt;99</td>
<td>94 (Creosol)</td>
<td>94 (Creosol)</td>
<td>Zhu et al. Green Chem. 2014, 16, 2636.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/SO$_2$H-MIL-101(Cr)</td>
<td>H$_2$O</td>
<td>1.0</td>
<td>90</td>
<td>1</td>
<td>100</td>
<td>98.4 (Creosol)</td>
<td>98.4 (Creosol)</td>
<td>Zhang et al. J. Mater. Chem. A. 2015, 3, 17008.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/STN@C</td>
<td>H$_2$O$^a$</td>
<td>0.34</td>
<td>100</td>
<td>6</td>
<td>100</td>
<td>45 (Creosol)</td>
<td>45 (Creosol)</td>
<td>Crossley et al. Science 2010, 327, 68.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/TiO$_2$@N-C</td>
<td>H$_2$O</td>
<td>1.0</td>
<td>150</td>
<td>6</td>
<td>95.5</td>
<td>&gt;99.5 (Creosol)</td>
<td>&gt;99.5 (Creosol)</td>
<td>Wang et al. ChemSusChem 2014, 7, 1537.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/POPO$^d$</td>
<td>IPA</td>
<td>1.0</td>
<td>140</td>
<td>18</td>
<td>96.5</td>
<td>98.2 (Creosol)</td>
<td>98.2 (Creosol)</td>
<td>Singuru et al. ChemCatChem 2017, 9, 2550.</td>
</tr>
<tr>
<td>Vanillin</td>
<td>Pd/PRGO$^e$/Ce-MOF</td>
<td>EtOH</td>
<td>1.0</td>
<td>100</td>
<td>5</td>
<td>100</td>
<td>&gt;99 (Creosol)</td>
<td>&gt;99 (Creosol)</td>
<td>Ibrahim et al. ChemCatChem. 2017, 9, 469.</td>
</tr>
<tr>
<td>Cinnamaldehyde</td>
<td>Pd/HHT$^g$</td>
<td>Dioxane</td>
<td>--</td>
<td>80</td>
<td>5</td>
<td>100</td>
<td>60.0 (Hydrocinnamaldehyde)</td>
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<td>Rao et al. Nature Comm., 2017, 8, 340.</td>
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<td>Wang et al. Tetrahedron, 2006, 62, 6107.</td>
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<td>Rao et al. Nature Comm., 2017, 8, 340.</td>
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$a$mixed with equal amount of decalin.  
$b$CM180 = carbonaceous microspheres-180 (hydrothermal temp.); $^c$SWNT= single-walled Nanotube; $^d$POP = porous organic polymer; $^e$PRGO = partially reduced graphene oxide; $^f$MMO = mixed metal Oxide; $^g$HHT = high heat-treated (for stacked cup carbon nanotubes); $^h$CB = carbon black; $^i$PMO = porous metal oxide.
The conversion (%) and selectivity (%) was calculated using the following formulae:

\[
\text{Conversion} \, (\%) = \frac{\text{mol of the reactant left}}{\text{initial mol of the reactant}} \times 100,
\]

\[
\text{Selectivity} \, (\%) = \frac{\text{mol of the product produced}}{\text{mol of the reactant consumed}} \times 100.
\]

Quantification of the selected products (mol%) from cinnamaldehyde was done using an Agilent Technologies 6890N equipped with an Rxi-5Sil MS as the column and a flame ionization detector (FID). External standards were prepared for 3,3-dimethoxypropyl benzene (DMPB), 2, 3-dihydroindenol (DHO), 1-allyl-4-methoxybenzene (AMB), and propenylbenzene (PNB) using MeOH as a solvent. The concentrations of the other peaks were quantified using the effective carbon number method (ECN), as proposed by Schofield. The formula to quantify the rest of the compounds is given as

\[
C_i = \frac{C_{\text{ref}}}{A_{\text{ref}}} \times \frac{A_i}{n_{\text{eff,ref}}} \times \frac{n_{\text{eff,i}}}{n_{\text{eff,ref}}},
\]

where \(C\) is the concentration, \(A\) is the area shown by the chromatogram in GC/FID, and \(n_{\text{eff}}\) is the effective carbon number. Index \(i\) and \(\text{ref}\) denote the selected compound with unknown concentration and reference, respectively. Depending on the structure of the compounds, toluene and hydrocinnamyl alcohol were used as references.
Calculation of metal dispersion, metal surface area and metal particle size of bimetallic Ga-Cu/HNZY catalyst using $\text{N}_2\text{O}$ pulse chemisorption

For monometallic

$$\text{Metal dispersion (D\%)} = \left( \frac{V \times S \times 1000}{22414 \times W} \right) \times 100 \times \left( \frac{A_w}{C/100} \right)$$

For bimetallic $A_w/C = M1 + M2$

$$\text{Metal dispersion (D\%)} = \left( \frac{V \times S \times 1000}{22414 \times W} \right) \times 100 \times \left( \frac{M1 + M2}{100} \right)$$

$$M1 = \left( \frac{C1}{C1 + C2} \right) \left( \frac{A_w1}{C1 + C2} \right)$$

$$M2 = \left( \frac{C2}{C1 + C2} \right) \left( \frac{A_w2}{C1 + C2} \right)$$

For monometallic

$$\text{Metal surface area (SA}_m\text{)} = \left( \frac{A \times B}{22414 \times W/1000} \right) \times 6.023 \times 10^{23} \times \left( \frac{A \times 10^{-16}}{C/100} \right)$$

For bimetallic,

$$A/C = (X1 + X2)$$

$$X1 = \left( \frac{C1}{C1 + C2} \right) \left( \frac{A1}{C1 + C2} \right)$$

$$X2 = \left( \frac{C2}{C1 + C2} \right) \left( \frac{A2}{C1 + C2} \right)$$

For monometallic

$$\text{Metal particle size (d}_p\text{)} = \left( \frac{6000}{SA_m \times \rho} \right)$$

For bimetallic,

$$\rho = (Y1 + Y2)$$

$$Y1 = \left( \frac{C1}{C1 + C2} \right) \rho1$$

$$Y2 = \left( \frac{C2}{C1 + C2} \right) \rho2$$
Fig. S2 XRD patterns of the Ga-doped Cu/HNZY (oxide form).
Fig. S3 XPS core-level spectra of the Cu 2p state of Cu-based catalysts (oxide form).
Fig. S4 High-magnification HR-TEM image of the 5C-2G catalyst. Yellow and red lines indicate the (202) and (111) lattice plane corresponding to Ga$_2$O$_3$ and Cu, respectively.
Fig. S5 High-magnification HRTEM image of the 10C–2G catalyst.
Fig. S6 (a) FE-SEM image, (b) –(g) elemental mapping of O, Al, Si, Cu, and Ga, respectively, and (h) corresponding EDS graph of the 10C–2G catalyst.
Fig. S7 Plausible reaction mechanism of cinnamaldehyde cyclization/hydrodeoxygenation to indane derivatives.
Fig. S8 (a) Molecular size of the adsorbates calculated by the ACD/3D software and (b) adsorption study of the adsorbates with 20 mg of adsorbent (CHZY and HNZY) at room temperature. The adsorption test showed that the adsorption capacity of the adsorbates was higher in the HNZY support as compared to the C-HZY support. (Note: pore channel size of typical zeolite-Y = 0.74 x 0.74 x 0.74 nm)
Fig. S9 GC-TOF/MS chromatograms of the liquid products obtained from the selective hydrogenation/hydrodeoxygenation of hydrocinnamaldehyde (HCAL, 2), cinnamyl alcohol (COL, 3), hydrocinnamyl alcohol (HCOL, 4) and 2,3-dihydroindanone (DHIO, 6) over the 10C–2G catalyst. Reaction conditions: 1 g feed, 35 ml MeOH, 0.25g catalyst, 1 h, 180 °C, and an initial H₂ pressure of 1 MPa.
Fig. S10  Recyclability test of the 10C-2G catalyst with high feed-to-catalyst ratio of 13.3:1
Reaction condition: 1 g vanillin, 0.075 g catalyst, 35 mL methanol, 160 °C, initial H₂ pressure of 1 MPa, and 2 h.
References