Supplementary Information for

Structure of catalytically active Rh-In bimetallic phase for amination of alcohols

Tsukasa Takanashi, Masazumi Tamura, Yoshinao Nakagawa* and Keiichi Tomishige*

Department of Applied Chemistry, School of Engineering, Tohoku University,
6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

*Corresponding authors: Keiichi Tomishige and Yoshinao Nakagawa

School of Engineering, Tohoku University,
6-6-07, Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

E-mail: tomi@erec.che.tohoku.ac.jp; yoshinao@erec.che.tohoku.ac.jp

Tel&fax: +81-22-795-7214
Table S1. Summary of XPS data of Rh-In/C (Rh 20 wt%)

<table>
<thead>
<tr>
<th>In/Rh</th>
<th>Binding energy / eV</th>
<th>Molar ratio from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rh 3d 5/2</td>
<td>Rh 3d 3/2</td>
</tr>
<tr>
<td>0.1</td>
<td>307.40</td>
<td>312.15</td>
</tr>
<tr>
<td>0.2</td>
<td>307.35</td>
<td>312.10</td>
</tr>
<tr>
<td>0.5</td>
<td>307.32</td>
<td>312.03</td>
</tr>
<tr>
<td>1</td>
<td>306.81</td>
<td>311.44</td>
</tr>
<tr>
<td>2^a</td>
<td>306.69</td>
<td>311.31</td>
</tr>
</tbody>
</table>

^a Actual value was 1.6 (XRF). ^b Large uncertainty exists because of the overlap between Rh 3d bands and the tail of C 1s bond (Fig. S6).
Fig. S1. XRD patterns of Rh-In/C (Rh 5 wt%) in N₂. Patterns in the regions shown in gray have noise because of the overlap with the signals for XRD cell (the signals for cell were removed by subtraction). (a) Rh/C; (b) In/Rh=0.1; (c) In/Rh=0.2; (d) In/Rh=0.5; (e) In/Rh=1; (f) In/Rh=1.5; (g) In/Rh=2. CO/Rh and TOF values are the reported ones in ref. S1.

Fig. S2. XRD patterns of In-Rh/C (Rh 20 wt%, In/Rh=1) before and after catalytic use.
Fig. S3. Results of Rh K-edge EXAFS analysis of Rh-In/C (Rh 20 wt%) and reference compounds. (I) \( k^2 \)-Weighted EXAFS oscillations. (II) Fourier filtered EXAFS data (solid line) and calculated data (dotted line). Fourier filtering range: 0.166-0.292 nm. (a) Rh foil, (b) \( \text{Rh}_2\text{O}_3 \), (c) Rh/C, (d-g) Rh-In/C. (d) In/Rh=0.1, (e) In/Rh=0.2, (f) In/Rh=0.5, (g) In/Rh=1.
Fig. S4. Results of In K-edge EXAFS analysis of Rh-In/C (Rh 20 wt%) and reference compounds. (I) $k^2$-Weighted EXAFS oscillations. (II) Fourier filtered EXAFS data (solid line) and calculated data (dotted line). Fourier filtering range: 0.126-0.279 nm. (a) In foil, (b) In$_2$O$_3$, (c) Rh foil, (d) Rh$_2$O$_3$, (e-i) Rh-In/C. (e) In/Rh=0.1, (f) In/Rh=0.2, (g) In/Rh=0.5, (h) In/Rh=1.
Fig. S5. TEM-EDX elemental mapping of Rh-In/C (20 wt% Rh, In/Rh=1).
Fig. S6. Wide-scan XPS data of Rh-In/C (20 wt% Rh, In/Rh=1).
Fig. S7. XANES spectra of Rh-In/C (20 wt% Rh) and reference compounds. The y-axis was normalized. The absolute edge is the position with the largest slope. All the data were taken successively in one machine time (total <4 h).