Supplementary Information for

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

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Table S1. Summary of XPS data of Rh-In/C (Rh 20 wt%)

In/Rh	Binding energy / eV						Molar ratio from XPS	
	Rh 3d 5/2	Rh 3d 3/2	In 3d 5/2		In 3d 3/2		In(0)/ In(III)	In/Rh[b]
			In(III)	In(0)	In(III)	In(0)		
0.1	307.40	312.15	444.58	-	452.14	-	0	0.19
0.2	307.35	312.10	444.46	-	452.00	-	0	0.37
0.5	307.32	312.03	444.74	443.90	452.28	451.49	1.0	0.96
1	306.81	311.44	444.70	443.78	452.22	451.33	1.9	1.6
2[a]	306.69	311.31	444.44	443.66	452.00	451.22	1.5	2.4

[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).

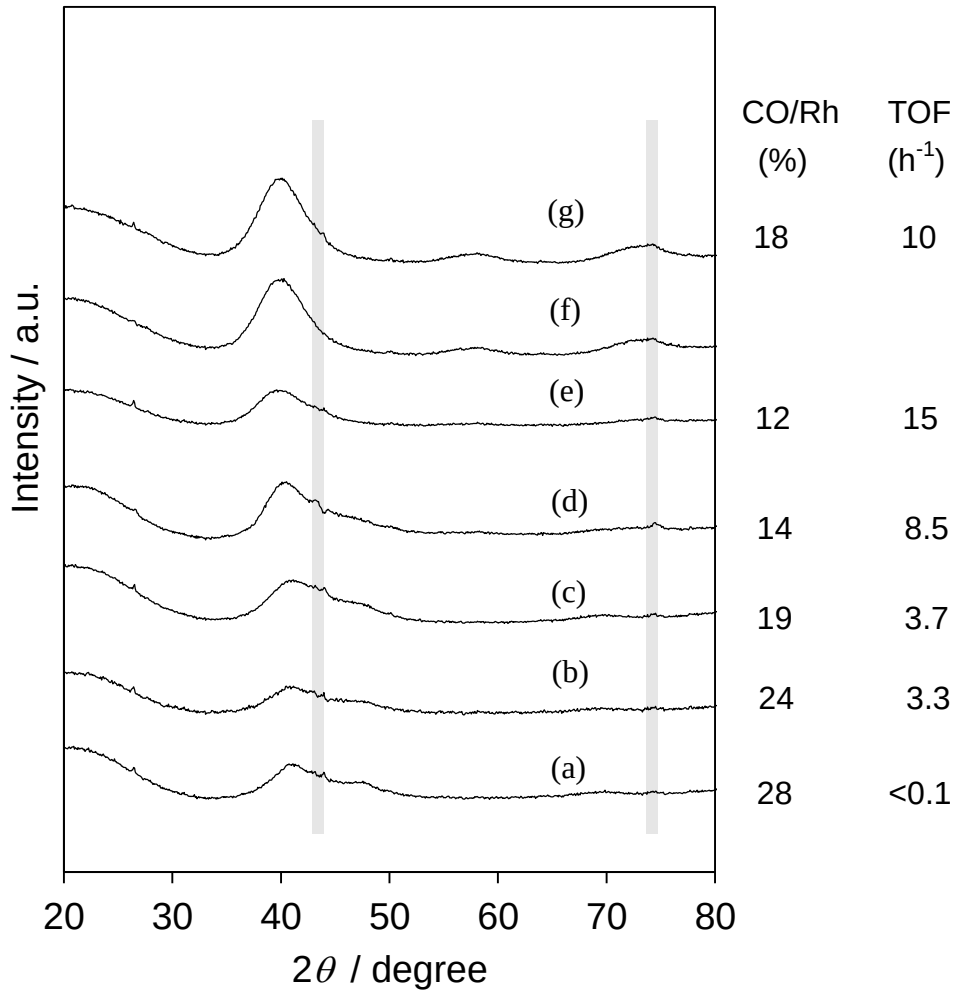

Fig. S1. XRD patterns of Rh-In/C (Rh 5 wt%) in N_2. Patterns in the regions shown in gray have noise because of the overlap with the signals for XRD cell (the signals for cell were removed by subtraction). (a) Rh/C; (b) In/Rh=0.1; (c) In/Rh=0.2; (d) In/Rh=0.5; (e) In/Rh=1; (f) In/Rh=1.5; (g) In/Rh=2. CO/Rh and TOF values are the reported ones in ref. S1.

[S1] T. Takanashi, Y. Nakagawa and K. Tomishige, *Chem. Lett.*, 2014, **43**, 822-824.

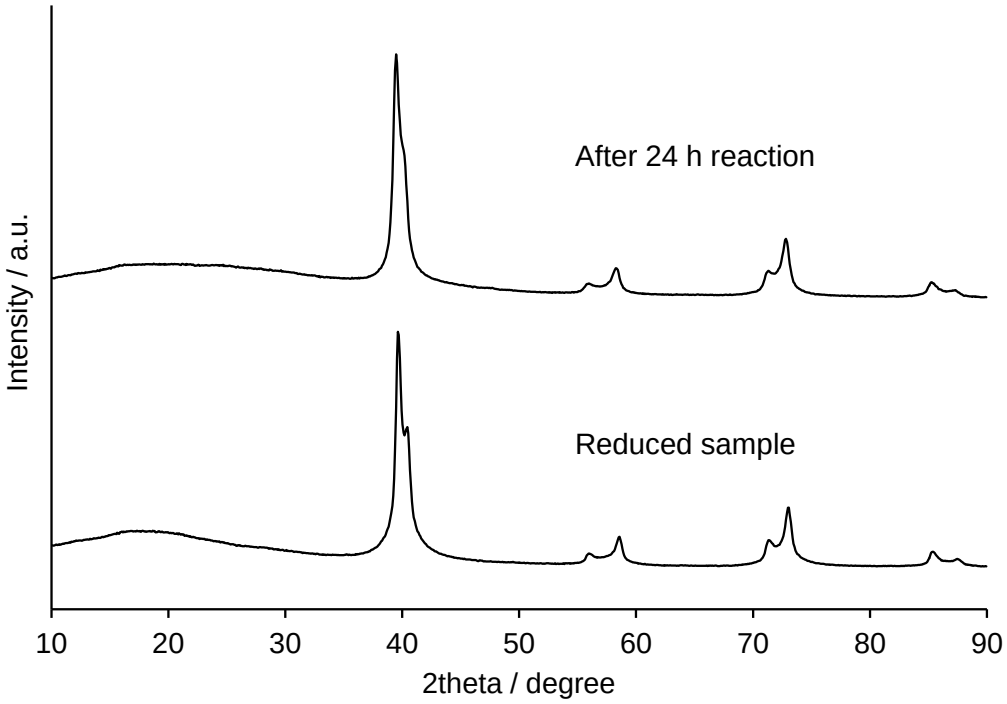

Fig. S2. XRD patterns of In-Rh/C (Rh 20 wt%, In/Rh=1) before and after catalytic use.

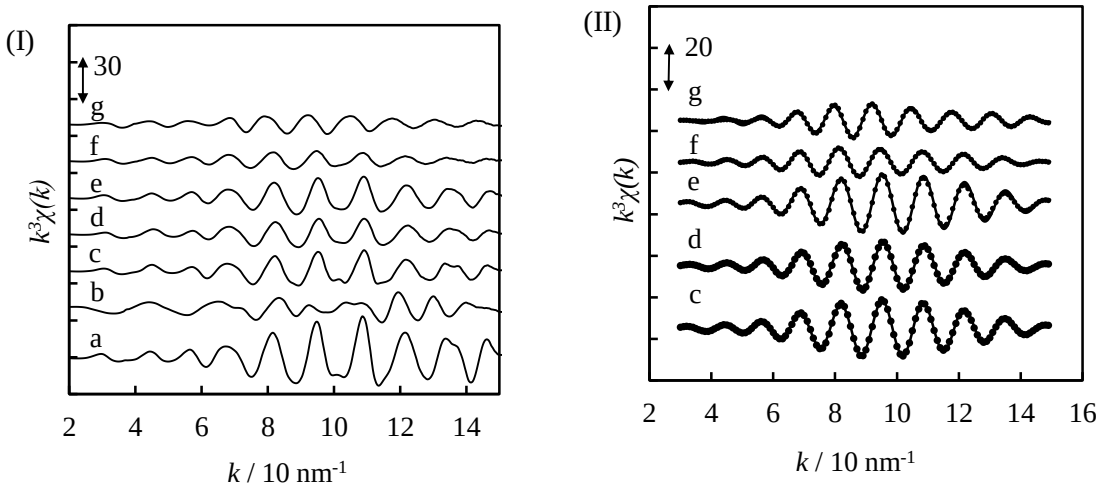

Fig. S3. Results of Rh *K*-edge EXAFS analysis of Rh-In/C (Rh 20 wt%) and reference compounds. (I) k^3-Weighted EXAFS oscillations. (II) Fourier filtered EXAFS data (solid line) and calculated data (dotted line). Fourier filtering range: 0.166-0.292 nm. (a) Rh foil, (b) Rh_2O_3, (c) Rh/C, (d-g) Rh-In/C. (d) In/Rh=0.1, (e) In/Rh=0.2, (f) In/Rh=0.5, (g) In/Rh=1.

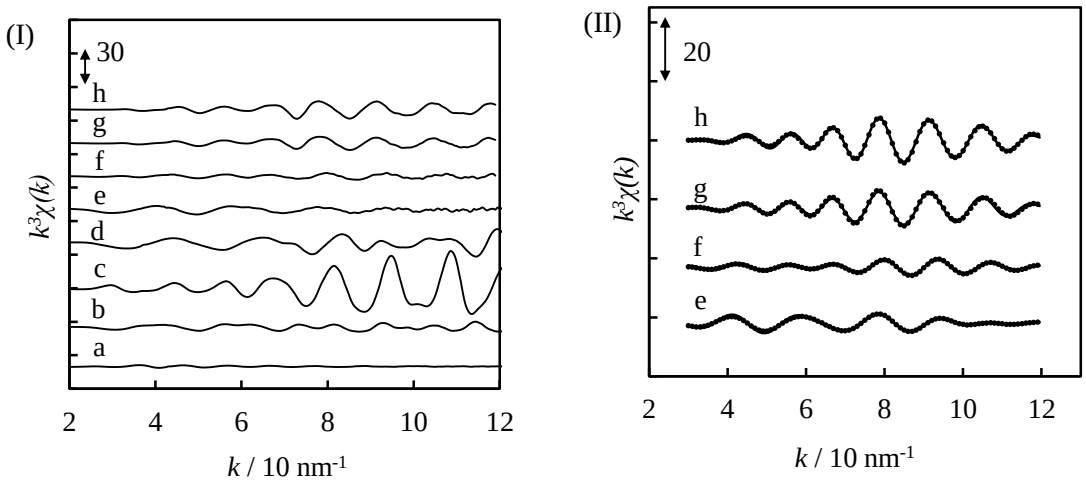

Fig. S4. Results of In *K*-edge EXAFS analysis of Rh-In/C (Rh 20 wt%) and reference compounds. (I) k^3-Weighted EXAFS oscillations. (II) Fourier filtered EXAFS data (solid line) and calculated data (dotted line). Fourier filtering range: 0.126-0.279 nm. (a) In foil, (b) In_2O_3, (c) Rh foil, (d) Rh_2O_3, (e-i) Rh-In/C. (e) In/Rh=0.1, (f) In/Rh=0.2, (g) In/Rh=0.5, (h) In/Rh=1.

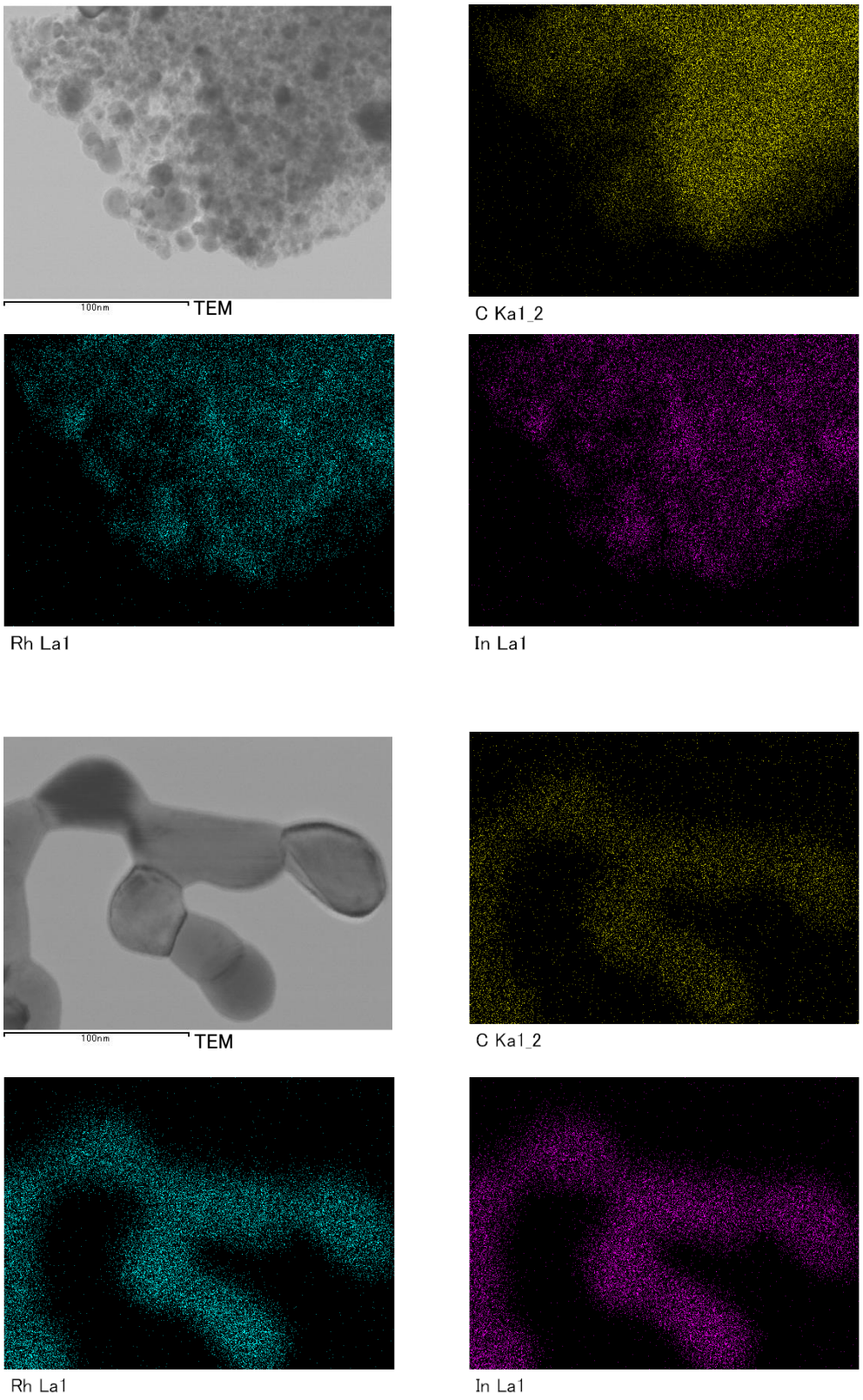

Fig. S5. TEM-EDX elemental mapping of Rh-In/C (20 wt% Rh, In/Rh=1).

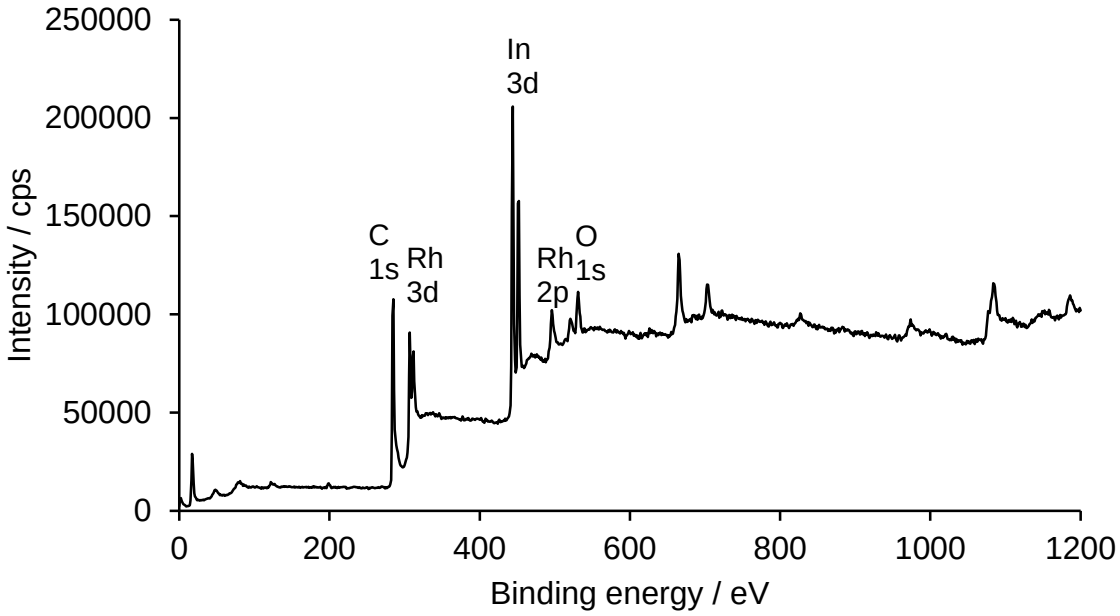

Fig. S6. Wide-scan XPS data of Rh-In/C (20 wt% Rh, In/Rh=1).

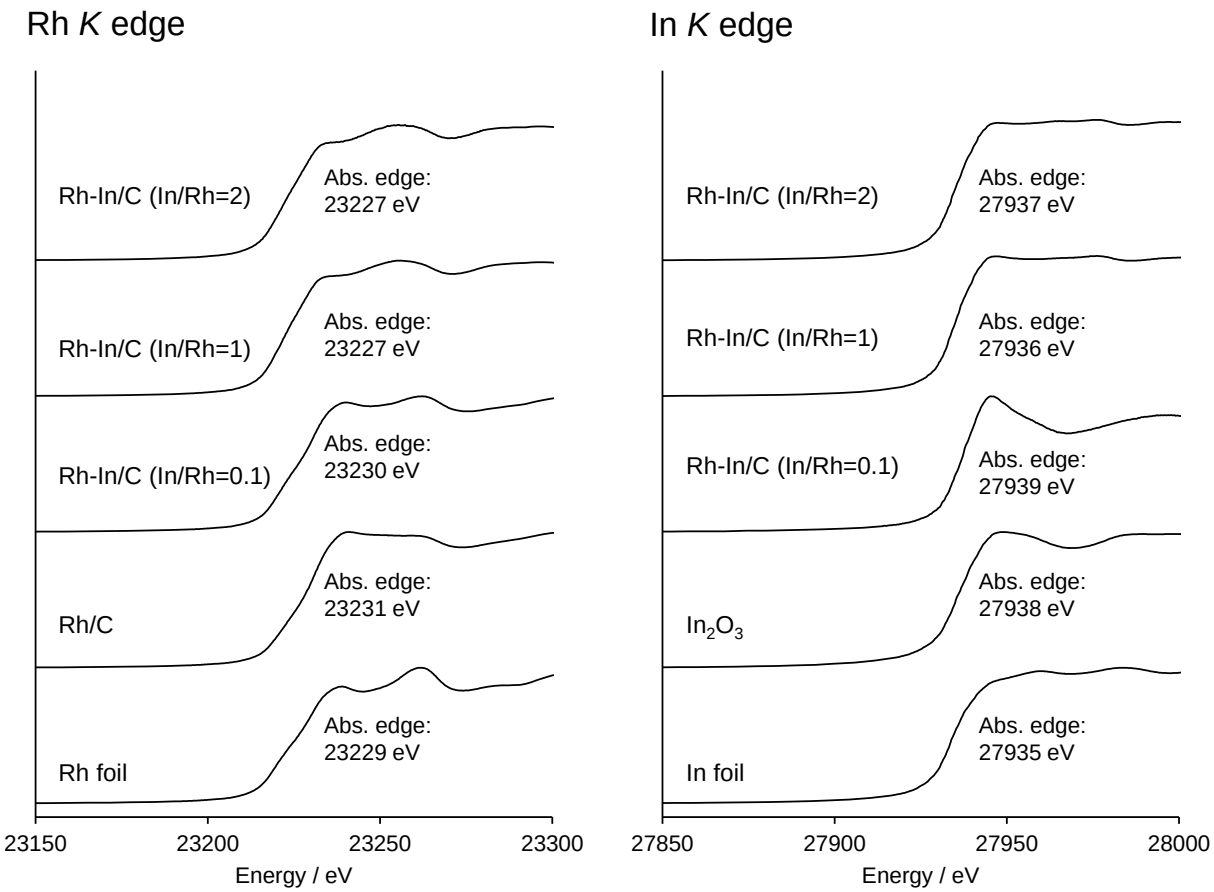

Fig. S7. XANES spectra of Rh-In/C (20 wt% Rh) and reference compounds. The y-axis was normalized. The absolute edge is the position with the largest slope. All the data were taken successively in one machine time (total <4 h).