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ELECTRONIC SUPPLEMENTARY INFORMATION

Formation and Nitrile Hydrogenation Performance of Ru Nanoparticles on a K-doped Al_2O_3 Surface

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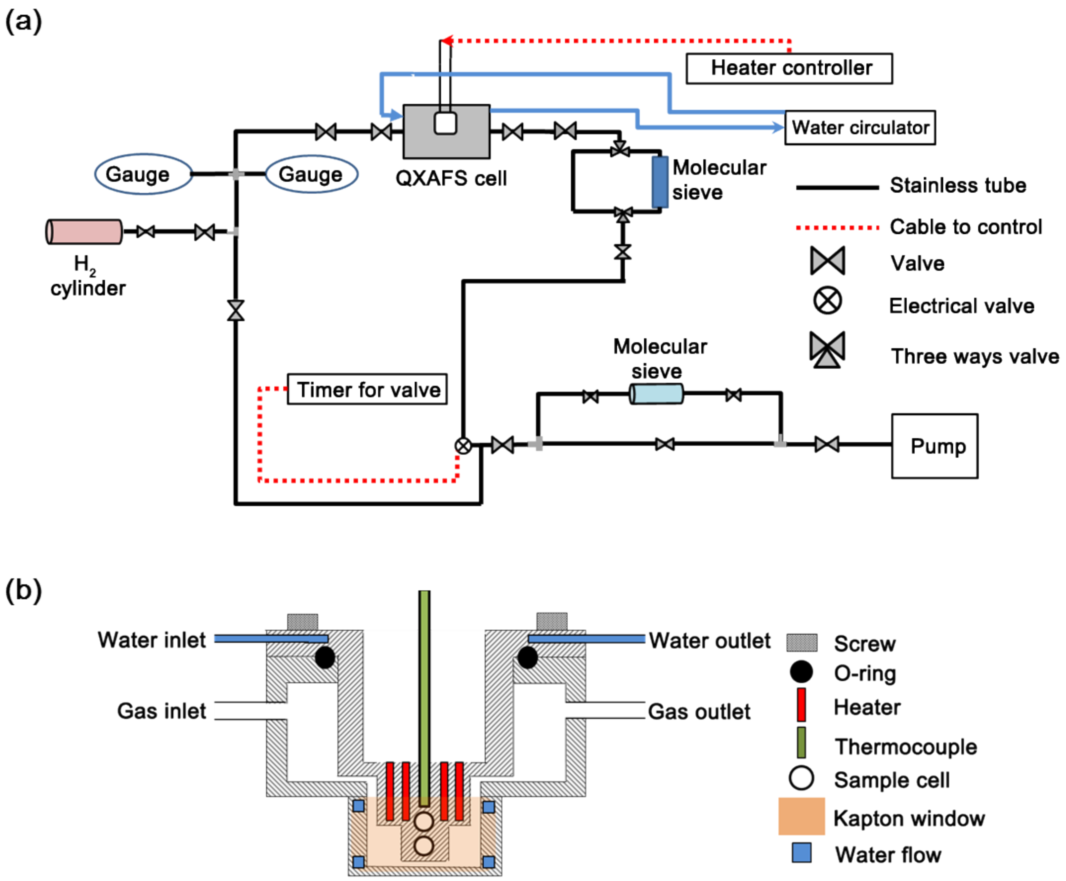


Fig. S1 (a) Setup for in situ QXAFS measurements and (b) side view of the in situ QXAFS cell.

Table S1 Curve-fitting results for Ru K-edge k^3-weighted EXAFS Fourier transforms of $Ru_3(CO)_{12}$ and $Ru_{3\text{-}CO}$/K-Alu C (K: 4 wt%, Ru: 4 wt%) during the decarbonylation process [a]

Sample (R factor)	Shell	CN	R /nm	ΔE_0 /eV	σ^2 /10^{-5} nm^2
(a) $Ru_3(CO)_{12}$ (R_f = 1.6%) [b]	Ru-C(O)	4.2 ± 0.9	0.194 ± 0.001	4 ± 2	3 ± 1
	Ru-Ru	1.8 ± 2.0	0.284 ± 0.004	-2 ± 11	4 ± 4
	Ru-(C)O	3.5 ± 1.3	0.305 ± 0.005	3 ± 5	4 ± 2
$Ru_{3\text{-}CO}$/K-Alu C (K: 4 wt%, Ru: 4 wt%)					
(b) at 298 K (R_f = 2.1 %) [c]	Ru-C(O)	3.0 ± 1.6	0.189 ± 0.002	-6 ± 7	4 ± 3
	Ru-Ru	1.0 ± 1.7	0.281 ± 0.004	-2 ± 9	3 ± 5
	Ru-(C)O	3.2 ± 2.3	0.299 ± 0.007	-6 ± 7	5 ± 4
(c) at 400 K (R_f = 2.2%) [c, d]	Ru-C(O)	3.1 ± 1.1	0.189 ± 0.001	0 ± 4	4 ± 2
	Ru-Ru	1.1 ± 0.4	0.281 ± 0.002	6 ± 5	4 ± 1
	Ru-(C)O	3.2 ± 1.2	0.299	1 ± 2	4 ± 2
(d) at 427 K (R_f = 2.9%) [c, d]	Ru-C(O)	3.3 ± 1.4	0.188 ± 0.002	-1 ± 6	5 ± 2
	Ru-Ru	1.4 ± 0.6	0.280 ± 0.002	3 ± 6	5 ± 2
	Ru-(C)O	3.6 ± 1.6	0.299	1 ± 2	5 ± 2
(e) at 519 K (R_f = 3.2%) [c, d]	Ru-C(O)	2.2 ± 0.9	0.187 ± 0.002	-1 ± 7	5 ± 2
	Ru-Ru	2.1 ± 0.8	0.276 ± 0.002	-1 ± 5	9 ± 1
	Ru-(C)O	2.6 ± 1.4	0.299	2 ± 2	5 ± 2
(f) at 621 K (R_f = 5.1%) [c, d, e]	Ru-C(O)	1.0 ± 0.3	0.187	1 ± 5	5
	Ru-Ru	2.7 ± 1.0	0.269 ± 0.001	0 ± 3	12 ± 2
	Ru-(C)O	1.2 ± 0.4	0.299	2 ± 3	5
(g) at 662 K (R_f = 6.7%) [f]	Ru-Ru	2.9 ± 0.6	0.267 ± 0.001	3 ± 2	10 ± 1
(h) at 703 K (R_f = 3.2%) [f]	Ru-Ru	3.7 ± 0.6	0.266 ± 0.001	2 ± 1	11 ± 1

[a] Fig. 2b. [b] Fig. 1c. k = 30–150 nm^{-1}, R = 0.105–0.320 nm. [c] k = 30–150 nm^{-1}, R = 0.130–0.320 nm. [d] R of Ru-(C)O in (c)–(f) was fixed at the value in (b). [e] R and σ^2 of Ru-C(O) in (f) were fixed at the values in (e). σ^2 of Ru-(C)O in (f) were fixed at the value in (e). [f] R = 0.160–0.320 nm. Ru-C/O could not be fitted.

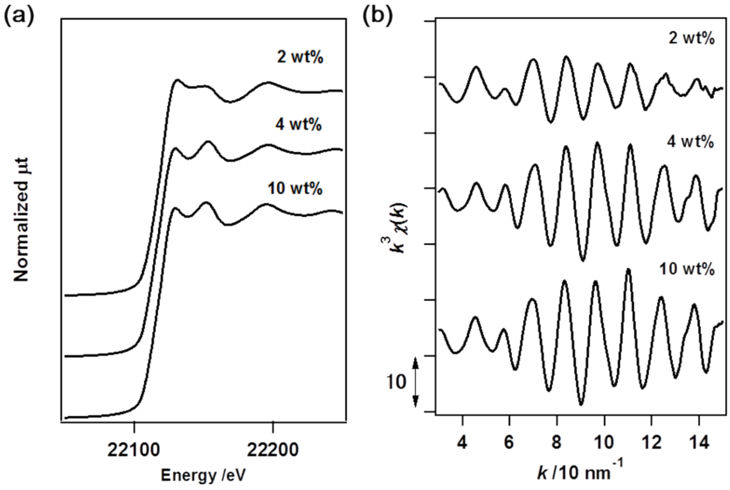


Fig. S2 (a) Ru K-edge XANES spectra and (b) Ru K-edge k^3-weighted EXAFS oscillations of $Ru_{3\text{-}CO}$/K-Alu C (K: 4 wt%, Ru: 2, 4, and 10 wt%) treated with dehydrated *n*-heptane under N_2 at 343 K for 20 min. XAFS spectra were measured at 20 K.

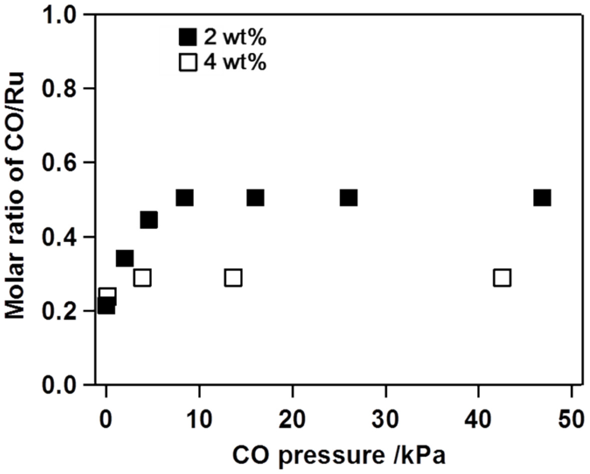


Fig. S3 Adsorption isotherms of CO on $Ru_{3\text{-}CO}$/K-Alu C (K: 4 wt%, Ru: 2 (■) and 4 (□) wt%) treated with dehydrated *n*-heptane under N_2 at 343 K for 20 min. CO adsorption was measured at 293–298 K.

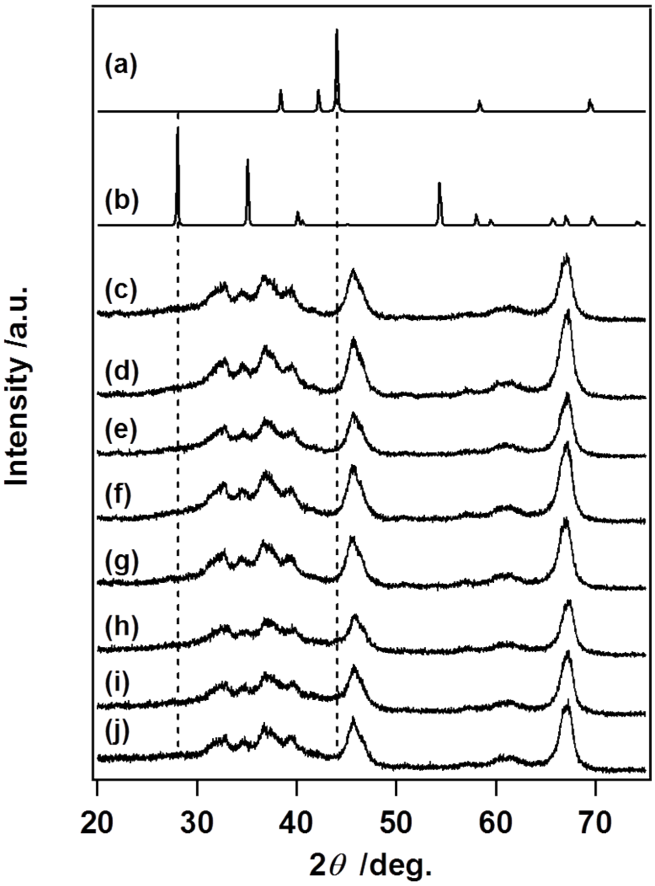


Fig. S4 XRD patterns of (a) Ru powder, (b) RuO_2, (c) Alu C, (d) K-Alu C (K: 4 wt%), (e) $Ru_{3\text{-CO}}$/K-Alu C (K: 4 wt%, Ru: 2wt%), (f) $Ru_{3\text{-CO}}$/K-Alu C treated with dehydrated *n*-heptane (K: 4wt%, Ru: 2wt%), (g) $Ru_{3\text{-CO}}$/K-Alu C after hydrogenation of valeronitrile in dehydrated *n*-heptane for 12 h (K: 4wt%, Ru 2wt%), (h) $Ru_{3\text{-CO}}$/K-Alu C (K: 4 wt%, Ru: 10wt%), (i) $Ru_{3\text{-CO}}$/K-Alu C treated with dehydrated *n*-heptane (K: 4 wt%, Ru: 10 wt%), and (j) $Ru_{3\text{-CO}}$/K-Alu C after hydrogenation of valeronitrile in dehydrated *n*-heptane for 16 h (K: 4 wt%, Ru: 10 wt%). Treatments with dehydrated *n*-heptane at 343 K were performed under N_2 for 20 min, and the valeronitrile hydrogenation was performed in dehydrated *n*-heptane at 343 K under H_2 at atmospheric pressure. The XRD patterns were recorded at 293–298 K under air.

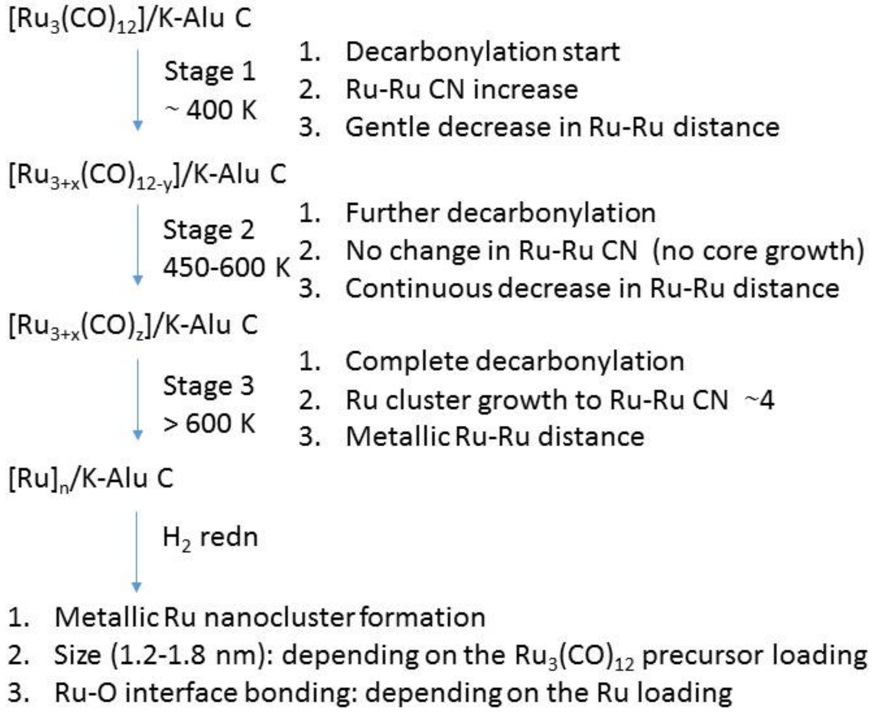


Fig. S5 Proposed three-stage structural transformations of the Ru carbonyl precursor on K-Alu C against the treatment temperatures and catalyst nanocluster structures formed by subsequent H_2 reduction.

Table S2 Curve-fitting results of Ru K-edge k^3-weighted EXAFS Fourier transforms of Ru_{acac}/K-Alu C and $Ru_{3\text{-}CO}$/oxide support (Ru: 2 wt%) after hydrogenation of valeronitrile in dehydrated *n*-heptane at 343 K for 12 h [a]

Sample (*R* factor) [b]	Shell	CN	*R* /nm	ΔE_0 /eV	σ^2 /10^{-5}nm^2
Ru_{acac}/K-Alu C (K: 4 wt%) (R_f = 1.1%)	Ru-O	2.2 ± 0.5	0.203 ± 0.002	6 ± 3	7 ± 2
	Ru-Ru	2.8 ± 0.4	0.264 ± 0.001	1 ± 2	9 ± 1
$Ru_{3\text{-}CO}$/MgO (R_f = 1.2%)	Ru-O	2.4 ± 0.9	0.204 ± 0.003	5 ± 5	9 ± 4
	Ru-Ru	4.0 ± 0.7	0.269 ± 0.001	5 ± 1	9 ± 1
$Ru_{3\text{-}CO}$/Alu C (R_f = 1.5%)	Ru-O	2.2 ± 0.6	0.204 ± 0.002	6 ± 4	8 ± 3
	Ru-Ru	2.5 ± 0.4	0.262 ± 0.001	1 ± 2	8 ± 1

[a] Fig. S6. [b] k = 30–150 nm^{-1}, R = 0.130–0.300 nm.

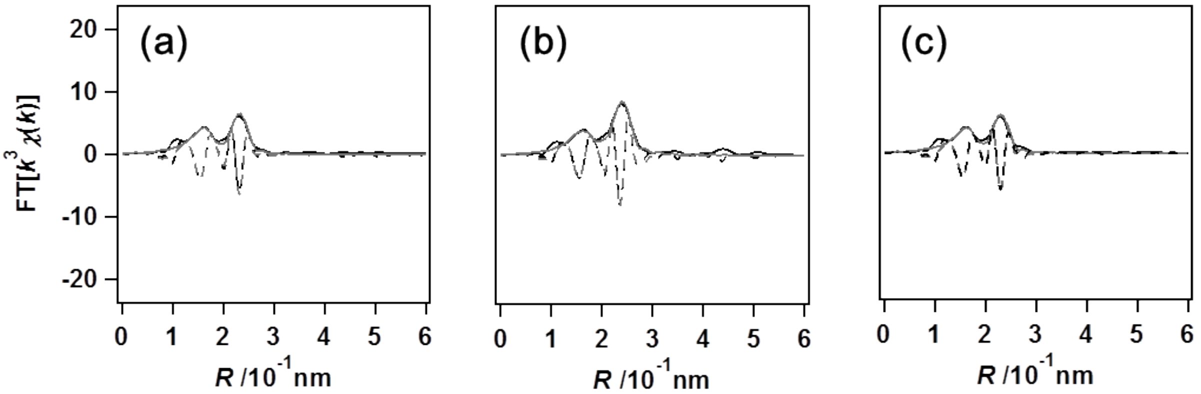


Fig. S6 Ru *K*-edge k^3-weighted EXAFS Fourier transforms of (a) Ru_{acac}/K-Alu C (K: 4 wt%, Ru: 2 wt%), (b) $Ru_{3\text{-}CO}$/MgO (Ru: 2 wt%), and (c) $Ru_{3\text{-}CO}$/Alu C (Ru: 2 wt%) after hydrogenation of valeronitrile in dehydrated *n*-heptane at 343 K under H_2 at atmospheric pressure for 12 h. XAFS spectra were measured at 20 K. Black and gray lines represent the observed and fitted data, respectively. Solid and dotted lines show absolute and imaginary parts, respectively.

Table S3 Low-energy adsorption modes of acetonitrile on the Ru surface. The h-f configuration is most favored, which is not affected by the layer number. The relative energies (kcal/mol) were measured from the most stable h-f configuration.

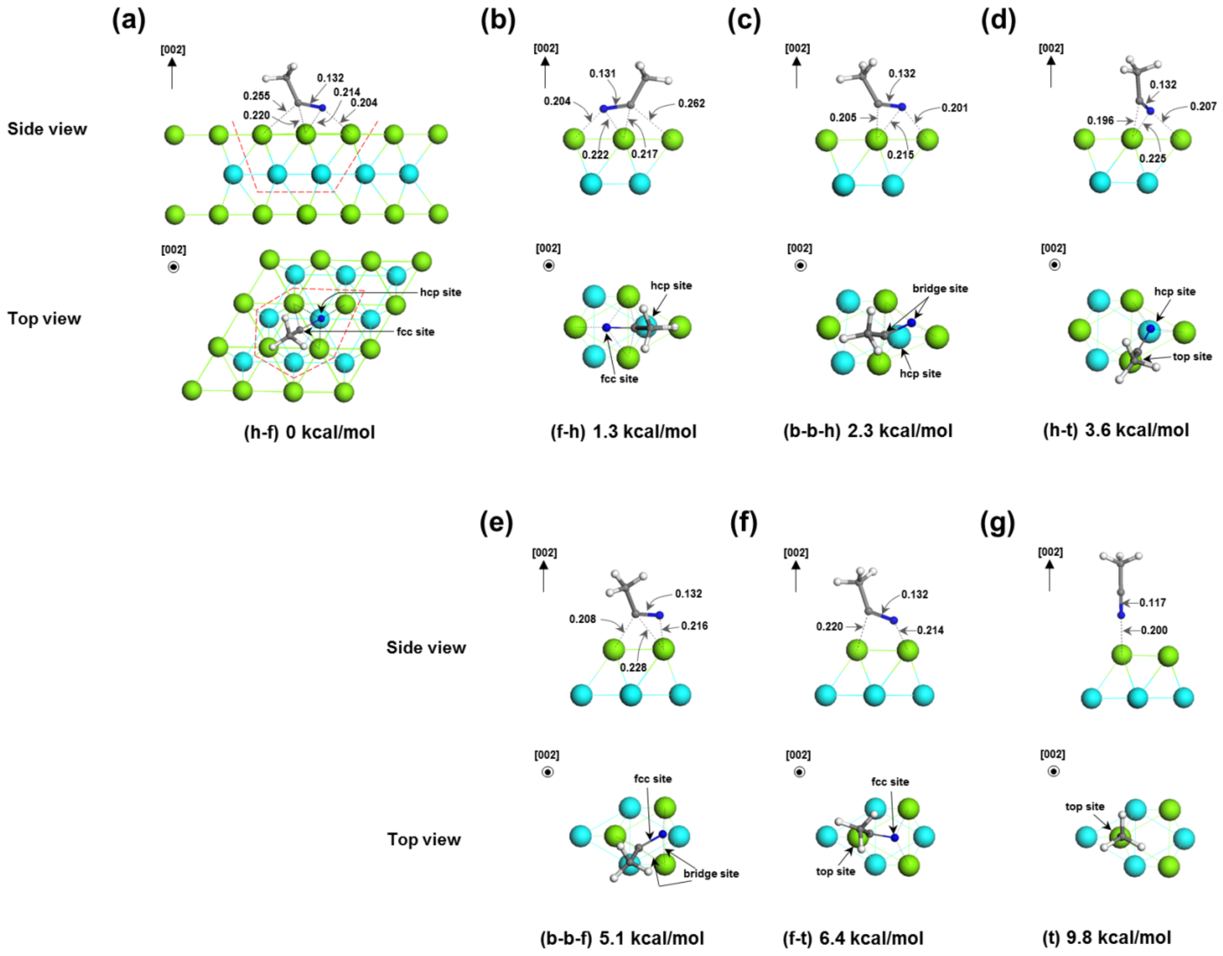
layer number[a]	h-f	f-h	b-b-h	h-t
3	0.0	1.3	2.3	3.6
4	0.0	1.9	1.9	3.5
5	0.0	2.0	2.0	3.5

[a] The bottom two layers were fixed at the corresponding bulk positions.

Table S4 Nitrene, carbene, and imine intermediates on the Ru surface. The nitrene intermediate is rather stable in energy compared with other intermediates, which is not affected by the layer number. The relative energies (kcal/mol) were measured from the most stable nitrene intermediate.

layer number[a]	nitrene	carbene	imine
3	0.0	8.3	10.4
4	0.0	9.5	11.8
5	0.0	10.6	12.5

[a] The bottom two layers were fixed at the corresponding bulk positions.



(h-f) 0 kcal/mol

(f-h) 1.3 kcal/mol

(b-b-h) 2.3 kcal/mol

(h-t) 3.6 kcal/mol

(b-b-f) 5.1 kcal/mol

(f-t) 6.4 kcal/mol

(t) 9.8 kcal/mol

Fig. S7 Side and top views of the adsorption structure of acetonitrile on the Ru surface; (a) h-f configuration, (b) f-h configuration, (c) b-b-h configuration, (d) h-t configuration, (e) b-b-f configuration, (f) f-t configuration, and (g) t configuration. The first term and the second term in the nomenclature represent the adsorption position of the nitrogen atom and the carbon atom of the CN group, respectively. The third term represents the position of the whole CN group. The positions on the Ru surface are abbreviated as follows: hcp site = h, fcc site = f, top site = t, bridge site that locates in the middle of Ru-Ru bond in the first layer = b. The relative energies were measured from the most stable h-f configuration. The C, N, H, and Ru atoms are colored in gray, blue, and white, respectively. Green and light blue spheres represent Ru atoms in the top (third) and second layers, respectively. Unit for bond distance is in nm.

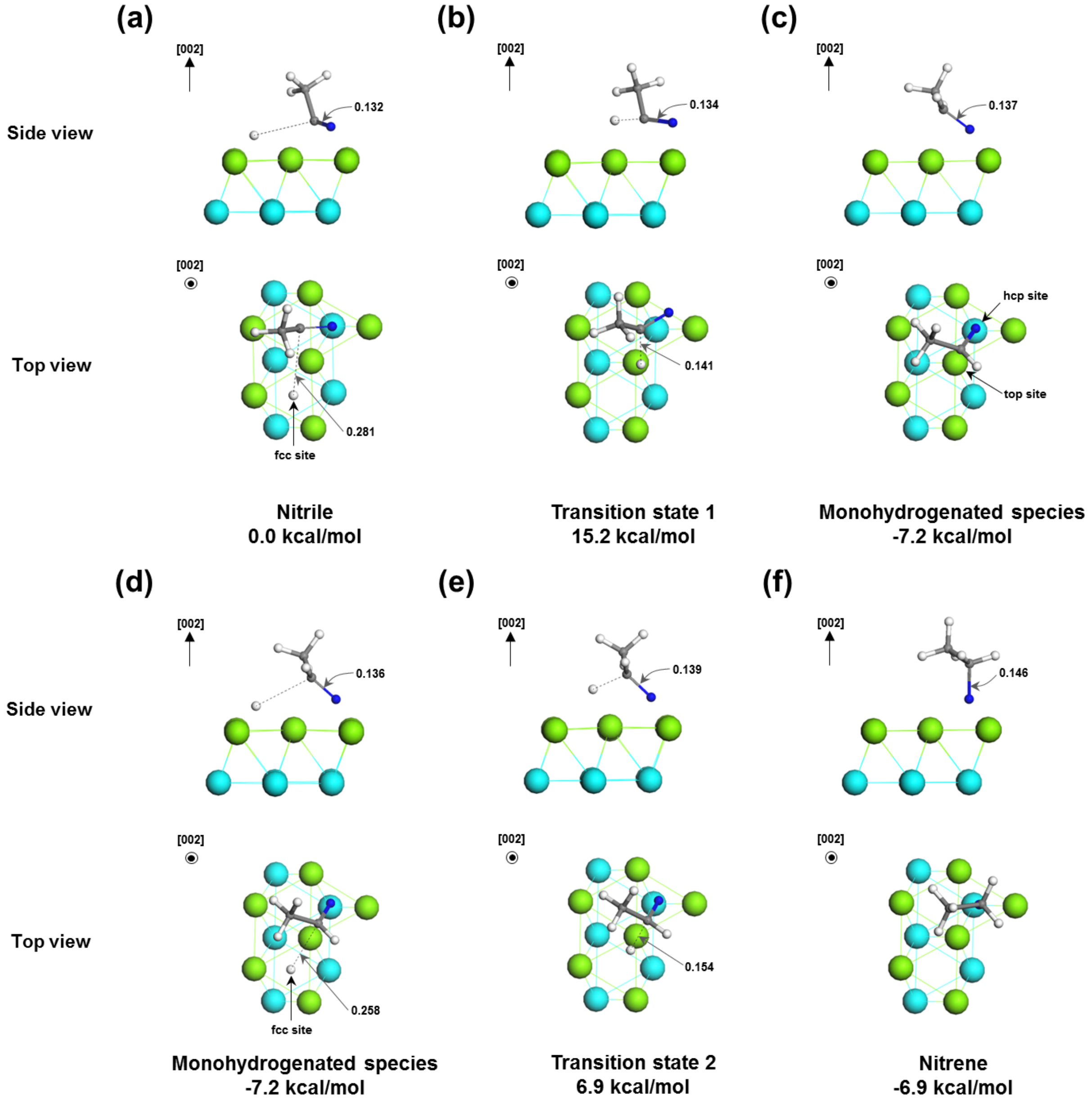


Fig. S8 Optimized structures and relative energies for the first (a-c) and second (d-f) hydrogenation of acetonitrile on the Ru surface. The relative energies were measured from the initial adsorption structure of acetonitrile on the Ru surface by h-f configuration. The C, N, H, and Ru atoms are colored in gray, blue, and white, respectively. Green and light blue spheres represent Ru atoms in the top (third) and second layers, respectively. Unit for bond distance is in nm.