Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Electronic Supplementary Information for

In-situ observation on the dynamic behaviors of Cu-Al-O_x catalyst for water gas shift reaction during daily start-up and shut-down (DSS)-like operation

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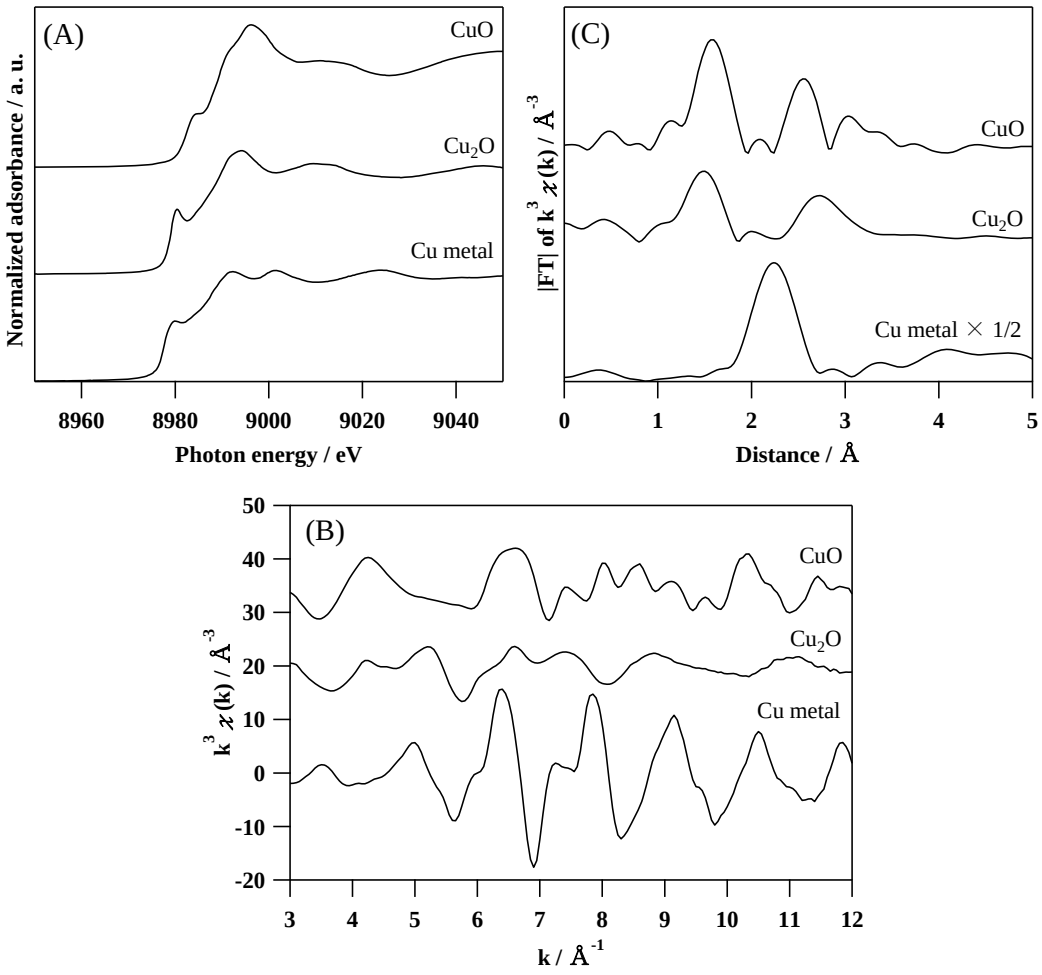

Figure S1 References spectra in the Cu-K edge XAFS measurement. (A) XANES spectra, (B) k^3-weighted EXAFS spectra ($k^3\chi(k)$), (C) Fourier transform of EXAFS spectra (|FT| of $k^3\chi(k)$).

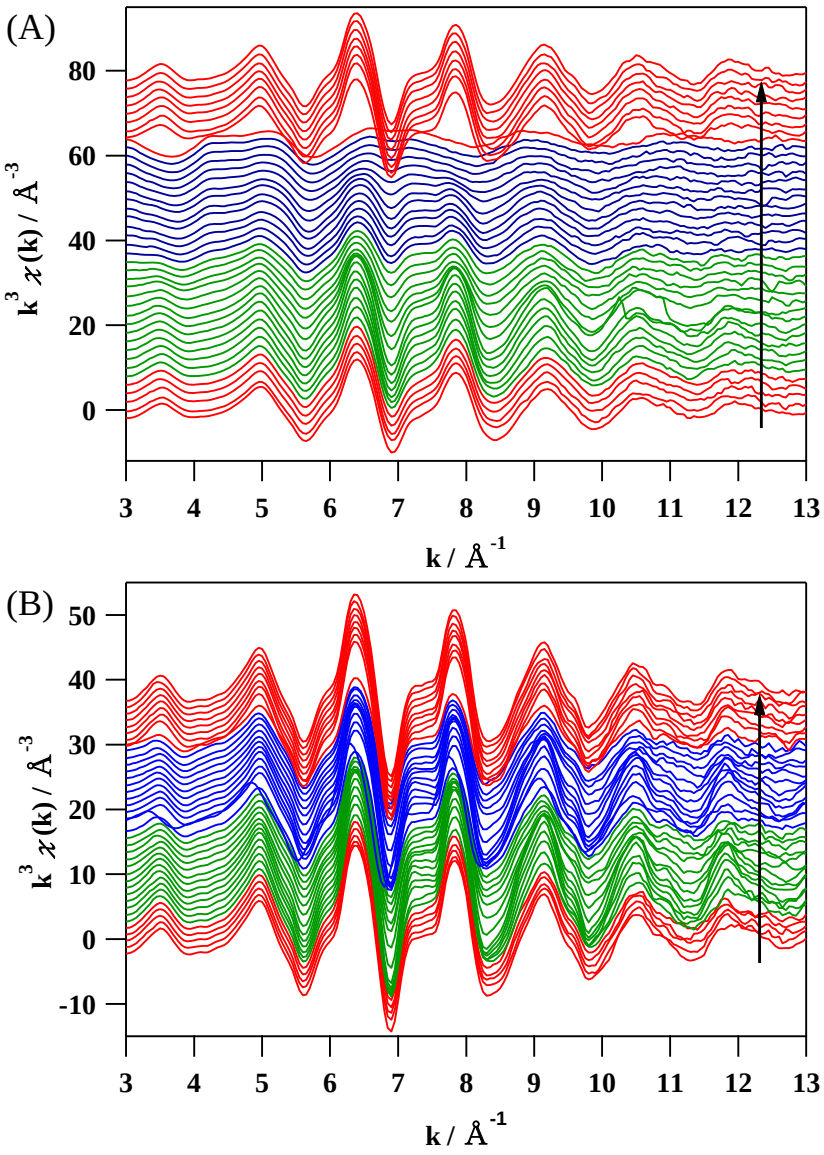

Figure S2 Changes in the k^3-weighted EXAFS spectra of (A) CP-Cu-Al-O_x and (B) IMP-Cu-Al-O_x during 2 cycles of DSS-like operations under the WGS reaction (red lines), 1st and 2nd DSS-like operation (green and blue lines).

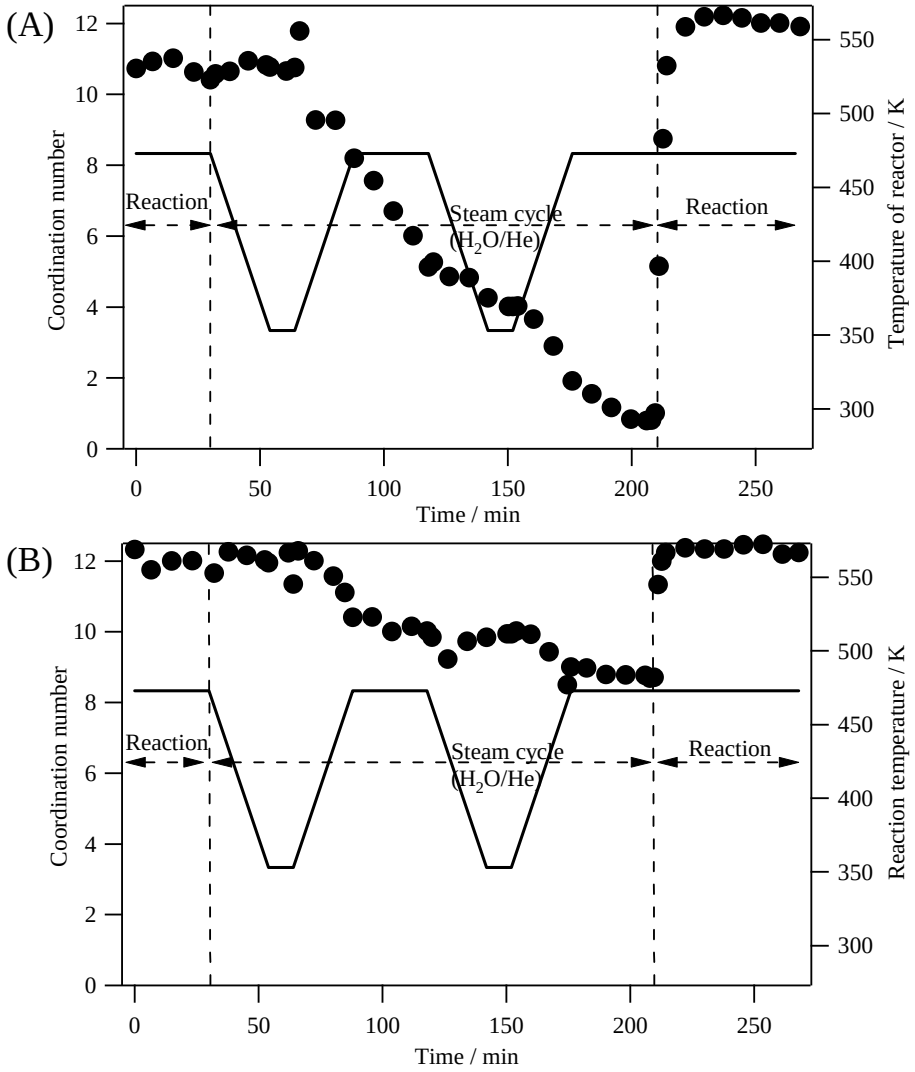

Figure S3 Changes in coordination number (CN) of the Cu-Cu at 2.24 Å (Cu metal) estimated from |FT| in Figure 4 over (A) CP-Cu-Al-O_x and (B) IMP-Cu-Al-O_x during 2 cycles of DSS-like operations.

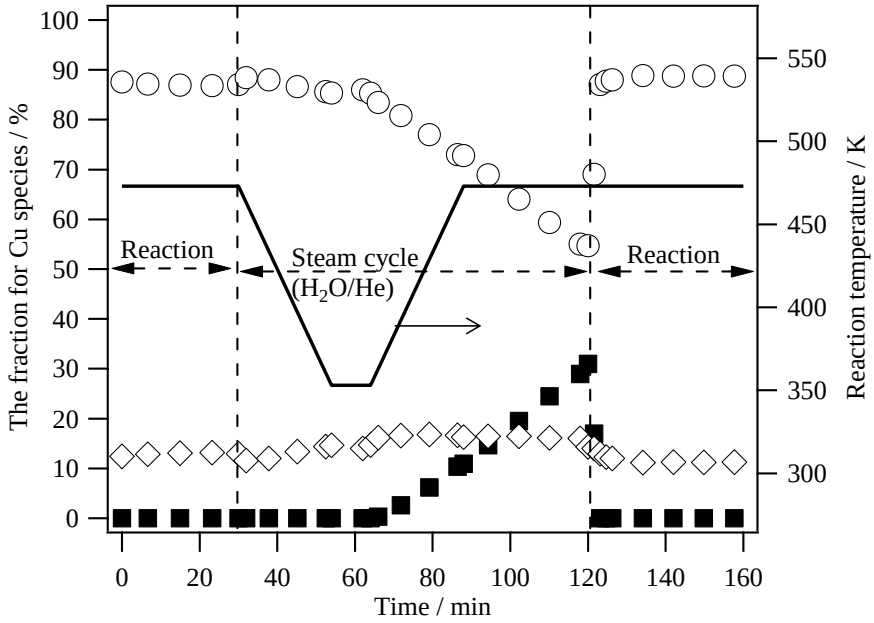

Figure S4 Fraction of Cu species over CP-Cu-Al-O_x during 1 cycle of DSS-like operation, (open circle) Cu^0, (close square) Cu^+ and (open diamond) Cu^{2+}. The steam cycle was performed between 353 and 473 K, which was different temperature from Figure 5(A).

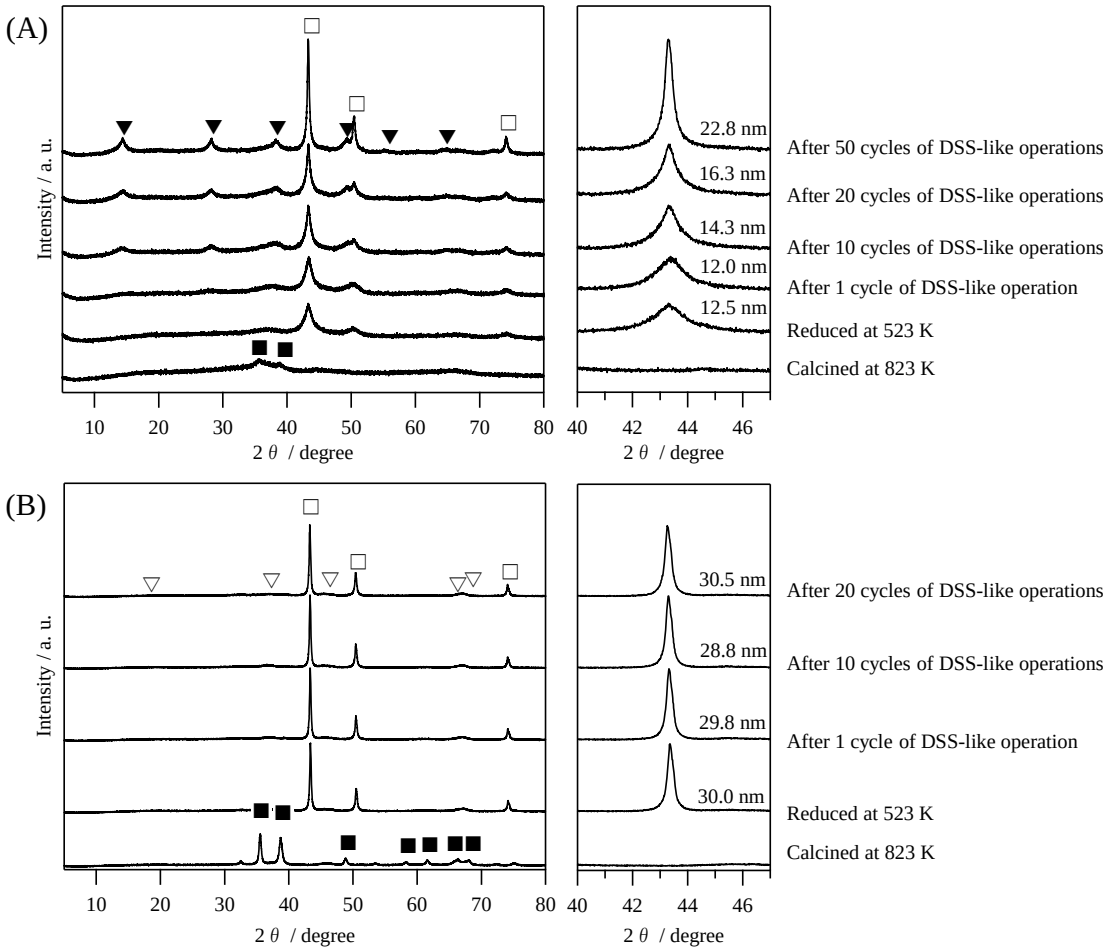

Figure S5 Changes in XRD patterns for the (A) CP- and (B) IMP-catalysts after calcination, reducion and DSS-like operations. (Close square) CuO, (open square) Cu, (close triangle) AlOOH (boehmite), and (open triangle) γ-Al_2O_3.

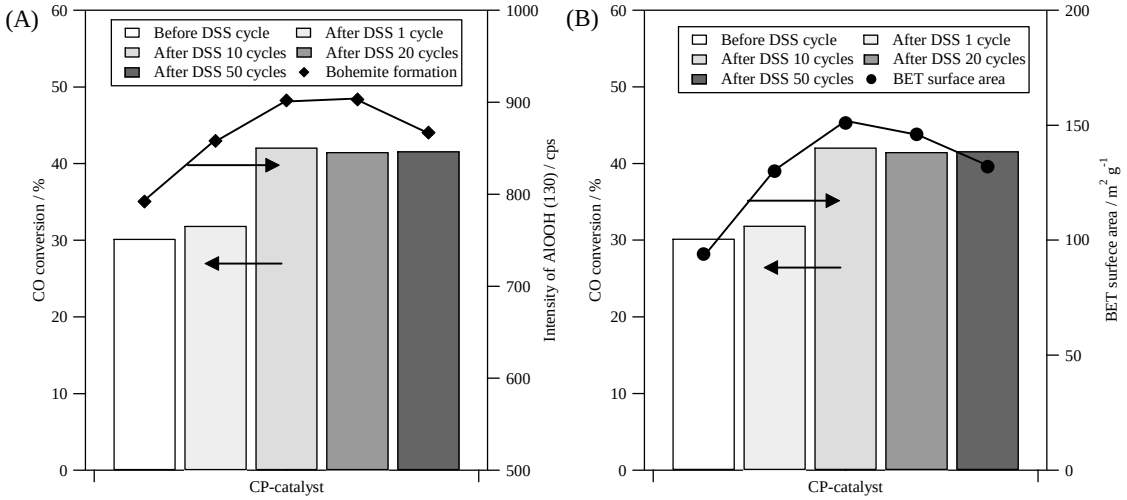

Figure S6 Relationships between CO conversion and (A) intensity of XRD patterns of boehmite (AlOOH) at (130) phase or (B) BET surface area against DSS-like operations of the CP-catalyst.

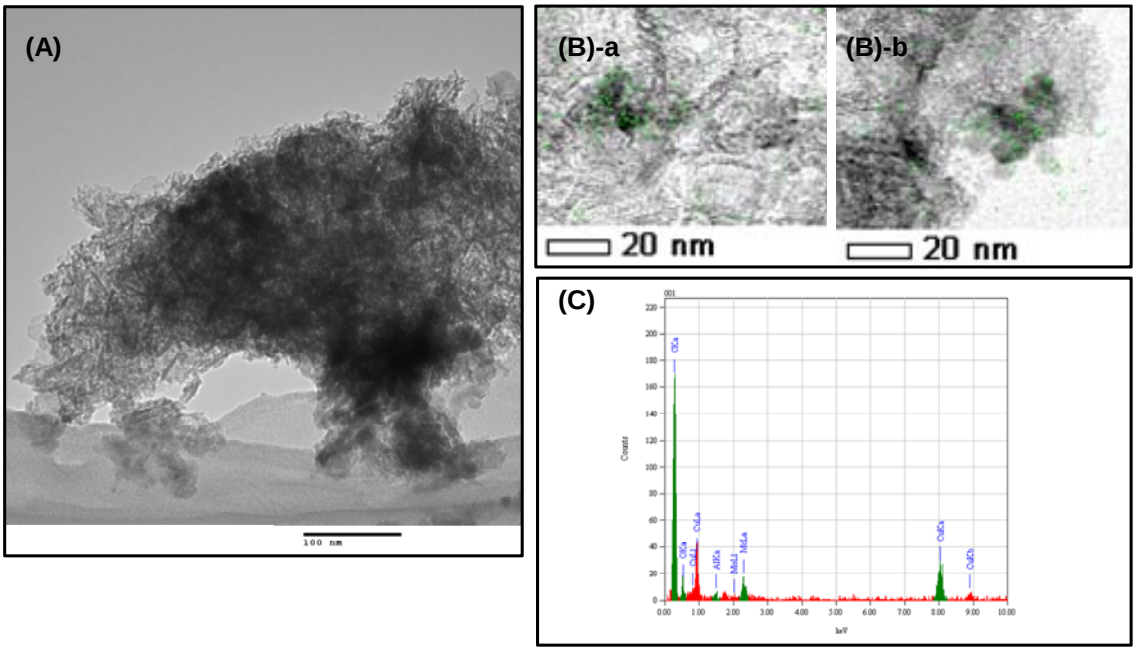

Figure S7 Morphology of CP-catalyst after DSS-like operations. (A) TEM image, (B) STEM-EDX mapping, (C) the result of element analysis of (B)-a. The green spots in (B) correspond to the presence of Cu element.

Table S1 CO conversion, reaction rate and surface areas of CP-Cu-Al-O_x, IMP-Cu-Al-O_x and MDC-7.

Catalysts	CO conversion / %		Reaction rate / mmol•min^{-1}		Cu^0 surface area / m^2•g^{-1}		BET surface area / m^2•g^{-1}	
	Before	After [a]	Before	After [a]	Before	After [a]	Before	After [a]
CP-catalyst	30.2	42.1	4.2×10^{-2}	5.8×10^{-2}	9.4	11.1	94	151
IMP-catalyst	24.8	2.3	3.4×10^{-2}	3.2×10^{-3}	3.1	1.2	87	92
MDC-7	58.9	45.8	8.1×10^{-2}	6.4×10^{-2}	18.5	10.7	49	47

[a] After 10 cycles of DSS-like operations.

Table S2 Summarized characters of CP-Cu-Al-O_x and IMP-Cu-Al-O_x before and after DSS-like operations.

Catalysts	Cu surface area (N_2O pulse)	Easily-oxidized Cu metal (*in-situ* XANES)	Easily-reduced CuO (H_2-TPR)	Cu (111) crystalline (XRD)	BET surface area (N_2 adsorption)	AlOOH
CP-catalyst	Increase	No changed	Increase (Gradual dispersed)	Growth	Increase	*In-situ* formation
IMP-catalyst	Decrease (Cu aggregation)	Decrease	Decrease (Crystallinity increase)	No changed	No changed	Not observed