Supporting Information for Self-Regeneration of Ni-Cu Alloy Catalyst during Three-Way Catalytic Reaction

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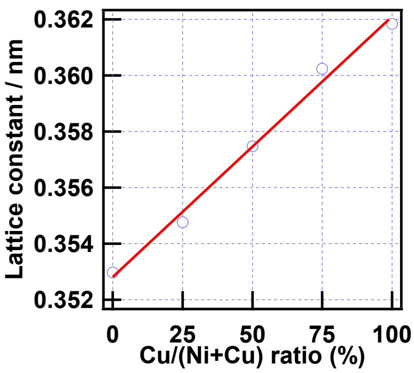

Figure S1 Relationship between the lattice constant estimated from the diffraction peak for (111) plane and Cu composition ratio.

The lattice constant was estimated by the following equation.

$$\frac{4\sin^2\theta}{\lambda^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For example, on the Ni/Al_2O_3,

$$\frac{4\sin^2(44.473°)}{0.15418^2} = \frac{1^2 + 1^2 + 1^2}{a^2}, a = 0.3528$$

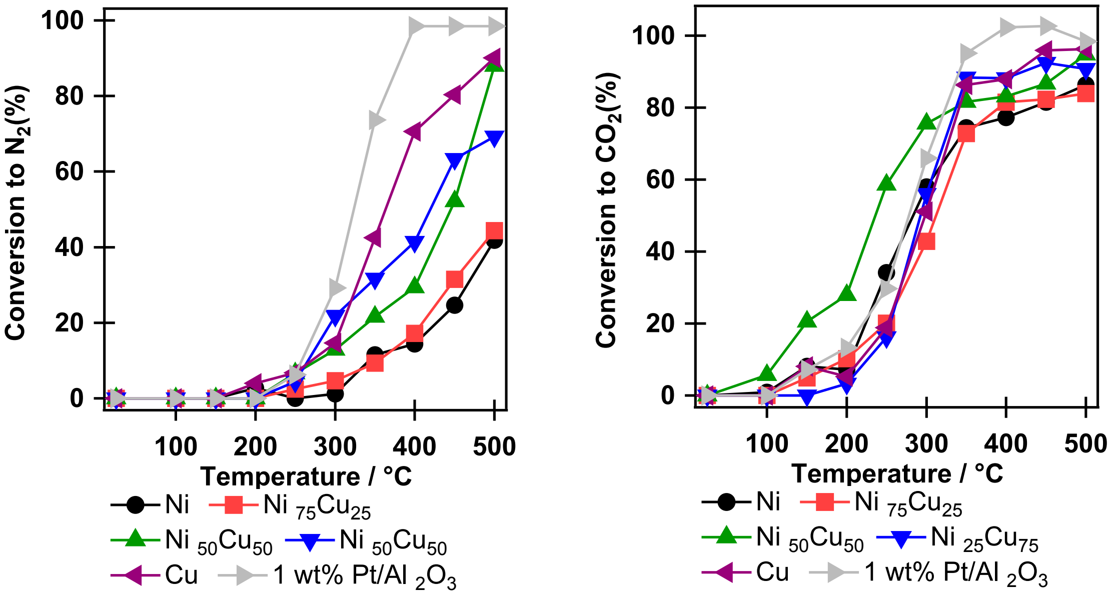

Figure S2 Conversion to N_2 (left) and CO_2 (right) during three-way catalytic reaction over 10 wt% Ni_xCu_y/Al_2O_3 (x:y = 100:0, 75:25, 50:50, 25:75, 0:100) and 1 wt% Pt/Al_2O_3 catalysts.

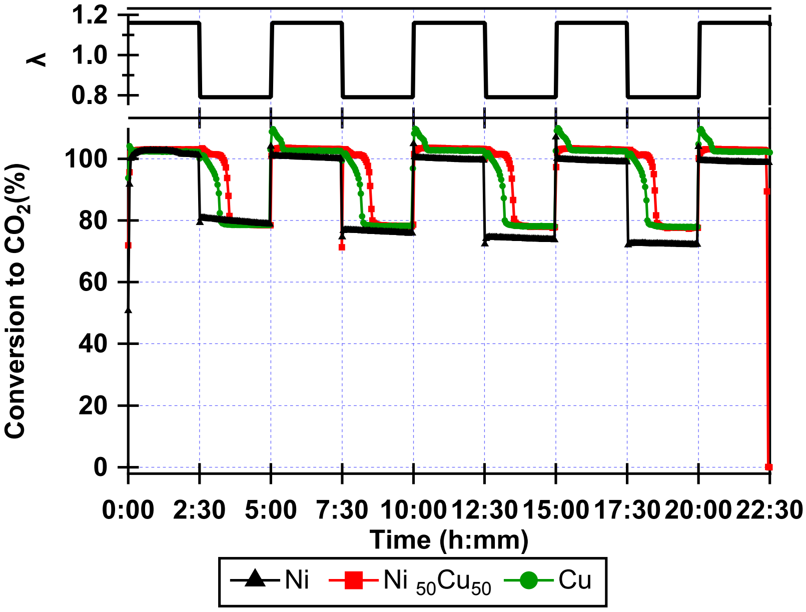

Figure S3 Temporal variation of conversion to CO_2 during three-way catalytic reaction 10 wt% Ni_xCu_y/Al_2O_3 (x:y = 100:0, 50:50, 0:100) and λ, an oxygen concentration indicator.

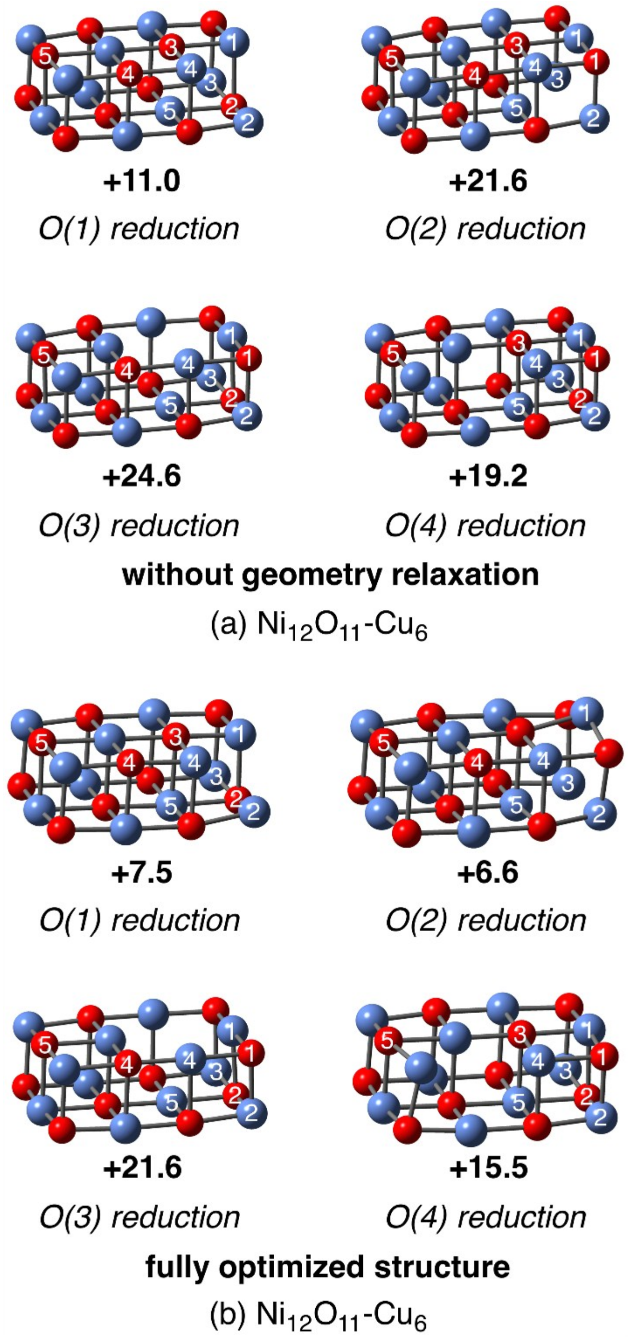

Figure S4 (a) Structures and reaction energies for reduction of (a) $Ni_{12}O_{11}$ without geometry relaxation[a)] and (b) fully optimized $Ni_{12}O_{11}$. Energies are kcal/mol, respectively.

[a)] Geometry was taken from the optimized $Ni_{12}O_{12}$ structure.

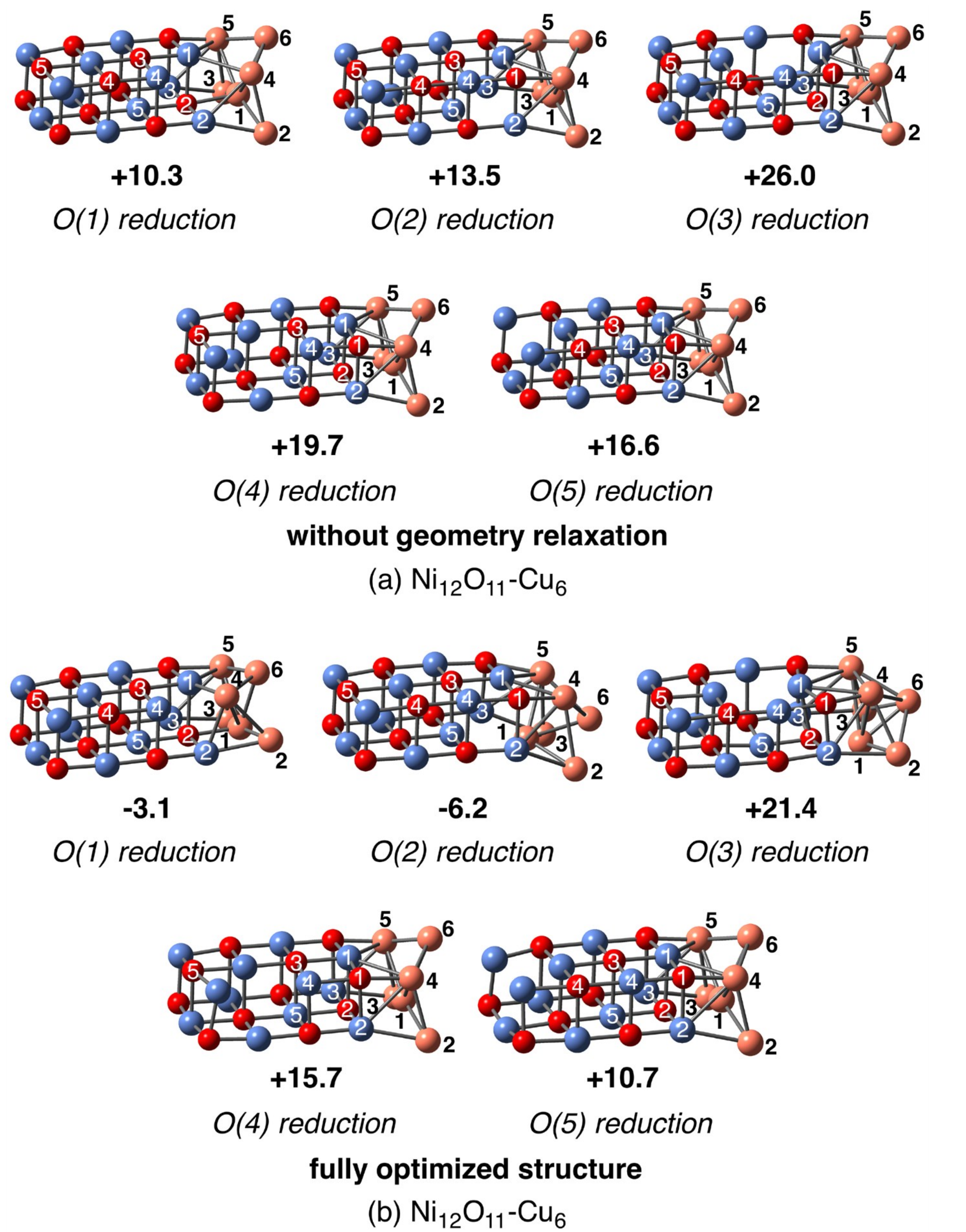

Figure S5 (a) Structures and reaction energies for reduction of (a) $Ni_{12}O_{11}$-Cu_6 without geometry relaxation [a)] and (b) fully optimized $Ni_{12}O_{11}$-Cu_6. Energies are kcal/mol, respectively.

[a)] Geometry was taken from the optimized $Ni_{12}O_{12}$-Cu_6 structure.

Table S1. Changes in important Ni(i)-Ni(j), Ni(i)-Cu(j), and Ni(i)-O(j) distances (in Å unit) and their Wiberg bond index (in parenthesis) upon CO reductions of $Ni_{12}O_{12}$ and $Ni_{12}O_{12}$-Cu_6.

(A) CO Reaction with O(1) of $Ni_{12}O_{12}$

	1	**2a**	**3a**
Ni(1)-Ni(2)	2.755 (0.03)	2.755 (0.29)	2.618 (0.31)
Ni(1)-Ni(3)	2.754 (0.03)	2.754 (0.03)	2.727 (0.03)
Ni(1)-Ni(4)	2.873 (0.02)	2.873 (0.23)	2.858 (0.18)
Ni(1)-Ni(5)	2.904 (0.02)	2.904 (0.03)	2.883 (0.03)
Ni(2)-Ni(3)	3.881 (0.01)	3.881 (0.02)	3.917 (0.02)
Ni(2)-Ni(4)	2.737 (0.03)	2.737 (0.33)	2.546 (0.38)
Ni(2)-Ni(5)	2.735 (0.03)	2.735 (0.04)	2.766 (0.03)
Ni(3)-Ni(5)	2.736 (0.03)	2.736 (0.03)	2.742 (0.03)
Ni(1)-O(1)	1.979 (0.37)	- -	
Ni(1)-O(2)	2.097 (0.25)	2.097 (0.25)	2.019 (0.28)
Ni(1)-O(3)	2.017 (0.23)	2.017 (0.21)	1.982 (0.23)
Ni(2)-O(2)	1.951 (0.31)	1.951 (0.26)	1.993 (0.24)

(B) CO Reaction with O(2) of $Ni_{12}O_{12}$

	1	**2b**	**3b**
Ni(1)-Ni(2)	2.755 (0.03)	2.755 (0.13)	2.885 (0.05)
Ni(1)-Ni(3)	2.754 (0.03)	2.754 (0.13)	2.885 (0.05)
Ni(1)-Ni(4)	2.873 (0.02)	2.873 (0.02)	2.840 (0.03)
Ni(1)-Ni(5)	2.904 (0.02)	2.904 (0.11)	3.244 (0.02)
Ni(2)-Ni(3)	3.881 (0.01)	3.881 (0.23)	2.799 (0.40)
Ni(2)-Ni(4)	2.737 (0.03)	2.737 (0.03)	2.802 (0.03)
Ni(2)-Ni(5)	2.735 (0.03)	2.735 (0.25)	2.458 (0.28)
Ni(3)-Ni(5)	2.736 (0.03)	2.736 (0.25)	2.458 (0.28)
Ni(1)-O(1)	1.979 (0.37)	1.979 (0.39)	1.869 (0.46)
Ni(1)-O(2)	2.097 (0.25)	- -	
Ni(1)-O(3)	2.017 (0.23)	2.017 (0.22)	2.005 (0.23)
Ni(2)-O(2)	1.951 (0.31)	- -	

(C) CO Reaction with O(1) of $Ni_{12}O_{12}$-Cu_6

	1-Cu	2a-Cu	3a-Cu
Ni(1)-Ni(2)	2.886 (0.04)	2.886 (0.20)	2.937 (0.13)
Ni(1)-Ni(3)	2.886 (0.04)	2.886 (0.04)	2.863 (0.04)
Ni(1)-Ni(4)	2.886 (0.03)	2.886 (0.13)	2.885 (0.12)
Ni(1)-Ni(5)	2.899 (0.03)	2.899 (0.03)	2.939 (0.03)
Ni(2)-Ni(3)	4.029 (0.01)	4.029 (0.02)	4.037 (0.02)
Ni(2)-Ni(4)	2.844 (0.02)	2.844 (0.16)	2.772 (0.13)
Ni(2)-Ni(5)	2.824 (0.03)	2.824 (0.03)	2.828 (0.03)
Ni(3)-Ni(5)	2.824 (0.03)	2.824 (0.03)	2.831 (0.02)
Cu(1)-Ni(1)	2.813 (0.11)	2.813 (0.18)	2.853 (0.15)
Cu(1)-Ni(2)	2.959 (0.14)	2.959 (0.18)	2.927 (0.15)
Cu(1)-Ni(3)	2.958 (0.14)	2.958 (0.14)	2.878 (0.14)
Cu(1)-Ni(5)	4.142 (0.01)	4.142 (0.01)	4.069 (0.01)
Cu(2)-Ni(2)	2.559 (0.31)	2.559 (0.31)	2.483 (0.40)
Cu(3)-Ni(3)	2.559 (0.31)	2.559 (0.31)	2.560 (0.32)
Cu(4)-Ni(1)	2.758 (0.09)	2.758 (0.25)	2.542 (0.30)
Cu(4)-Ni(2)	2.655 (0.14)	2.655 (0.28)	2.449 (0.32)
Cu(4)-Ni(4)	3.941 (0.01)	3.941 (0.08)	2.641 (0.25)
Cu(5)-Ni(1)	2.759 (0.09)	2.758 (0.10)	2.602 (0.16)
Cu(5)-Ni(3)	2.655 (0.14)	2.655 (0.14)	2.745 (0.12)
Cu(6)-Ni(1)	3.230 (0.10)	3.230 (0.12)	2.571 (0.32)
Ni(1)-O(1)	2.027 (0.26)	- -	
Ni(1)-O(2)	2.062 (0.20)	2.062 (0.19)	2.079 (0.19)
Ni(1)-O(3)	2.019 (0.21)	2.019 (0.19)	2.012 (0.21)
Ni(2)-O(2)	2.014 (0.21)	2.014 (0.19)	2.008 (0.21)
Cu(1)-O(2)	2.146 (0.13)	2.146 (0.12)	2.087 (0.13)
Cu(4)-O(1)	1.985 (0.22)	- -	

(D) CO Reaction with O(2) of $Ni_{12}O_{12}$-Cu_6

	1-Cu	**2b-Cu**	**3b-Cu**
Ni(1)-Ni(2)	2.886 (0.04)	2.886 (0.14)	2.982 (0.07)
Ni(1)-Ni(3)	2.886 (0.04)	2.886 (0.14)	2.982 (0.07)
Ni(1)-Ni(4)	2.886 (0.03)	2.886 (0.03)	2.843 (0.03)
Ni(1)-Ni(5)	2.899 (0.03)	2.899 (0.11)	2.817 (0.07)
Ni(2)-Ni(3)	4.029 (0.01)	4.029 (0.08)	4.296 (0.03)
Ni(2)-Ni(4)	2.844 (0.02)	2.844 (0.02)	2.799 (0.03)
Ni(2)-Ni(5)	2.824 (0.03)	2.824 (0.11)	2.836 (0.07)
Ni(3)-Ni(5)	2.824 (0.03)	2.824 (0.11)	2.836 (0.07)
Cu(1)-Ni(1)	2.813 (0.11)	2.813 (0.22)	2.694 (0.23)
Cu(1)-Ni(2)	2.959 (0.14)	2.959 (0.27)	2.444 (0.38)
Cu(1)-Ni(3)	2.958 (0.14)	2.958 (0.27)	2.444 (0.38)
Cu(1)-Ni(5)	4.142 (0.01)	4.142 (0.07)	2.968 (0.16)
Cu(2)-Ni(2)	2.559 (0.31)	2.559 (0.29)	2.624 (0.21)
Cu(3)-Ni(3)	2.559 (0.31)	2.559 (0.29)	2.624 (0.21)
Cu(4)-Ni(1)	2.758 (0.09)	2.758 (0.11)	2.479 (0.16)
Cu(4)-Ni(2)	2.655 (0.14)	2.655 (0.15)	2.737 (0.10)
Cu(4)-Ni(4)	3.941 (0.01)	3.941 (0.01)	4.080 (0.01)
Cu(5)-Ni(1)	2.758 (0.09)	2.758 (0.11)	2.479 (0.16)
Cu(5)-Ni(3)	2.655 (0.14)	2.655 (0.15)	2.737 (0.10)
Cu(6)-Ni(1)	3.230 (0.10)	3.230 (0.10)	3.983 (0.05)
Ni(1)-O(1)	2.027 (0.26)	2.027 (0.23)	2.025 (0.27)
Ni(1)-O(2)	2.062 (0.20)	- -	
Ni(1)-O(3)	2.019 (0.21)	2.019 (0.19)	1.980 (0.22)
Ni(2)-O(2)	2.014 (0.21)	- -	
Cu(1)-O(2)	2.146 (0.13)	- -	
Cu(4)-O(1)	1.985 (0.22)	1.985 (0.21)	2.155 (0.15)