Supporting Information

for

Phyllosilicates-derived CuNi/SiO_2 catalysts in the selective hydrogenation of adipic acid to 1,6-hexandiol

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Numbers of figures: 11
Numbers of tables: 2

Activity Evaluation

The definition of conversion of reactant was defined as below:

$$\text{Conversion of reactnat (\%)} = \frac{\text{Moles of reactant consumed}}{\text{Moles of reactant fed in}} \times 100\% \qquad \text{(Eq. S1)}$$

In this study, adipic acid (AA), succinic acid (SUC), glutaric acid (GLU), butyric acid (BTA), pentanoic acid (PTA) and hexanoic acid (HXA) were tested as the reactants.

The definitions of selectivity and yield are as below:

$$\text{Selectivity of product } i \text{ (\%)} = \frac{\text{Moles of product } i \text{ formed}}{\text{Sum of moles of all product formed}} \times 100\% \qquad \text{(Eq. S2)}$$

$$\text{Yield of product } i \text{ (\%)} = \frac{\text{Moles of product } i \text{ formed}}{\text{Moles of reactant fed in}} \times 100\% \qquad \text{(Eq. S3)}$$

To reveal the intrinsic activity of selective hydrogenation, the TOF was calculated as:

$$\text{TOF} = \frac{\text{Moles of reactant consumed}}{\text{(Time, h)} \times \text{(Moles of the sum of } Cu^0 \text{ and } Cu^+\text{)}} \qquad \text{(Eq. S4)}$$

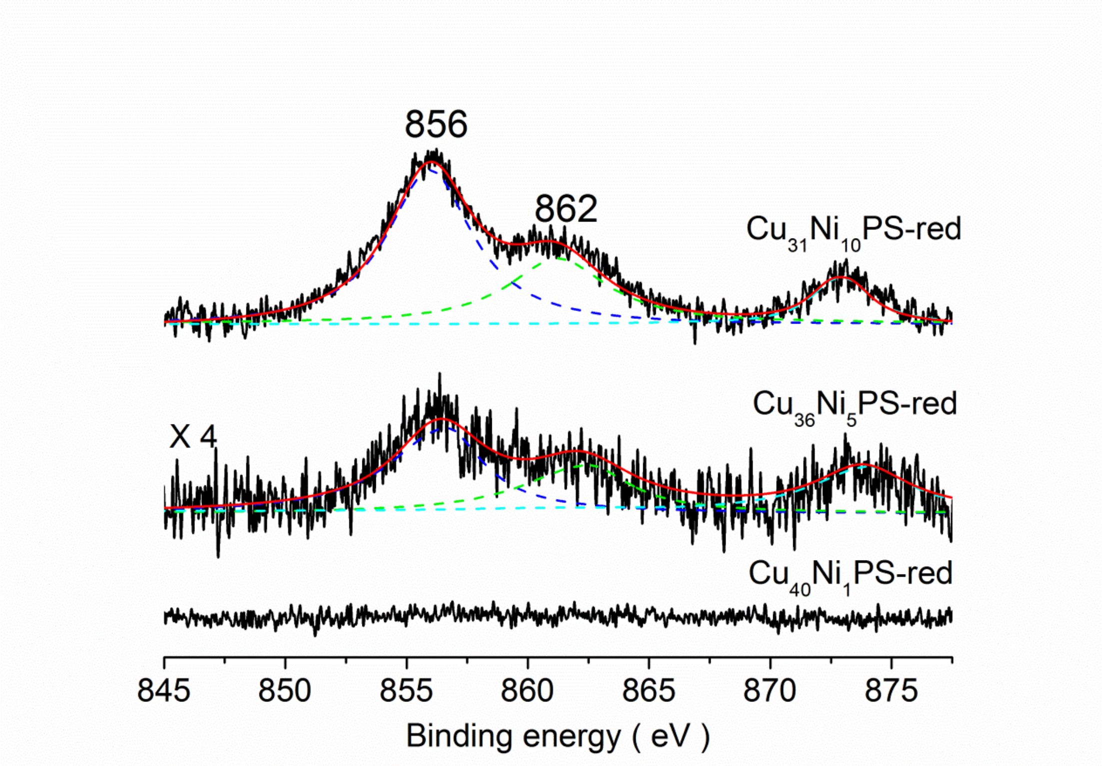


Figure S1. XPS spectra of Ni 2p core level of $Cu_xNi_{41-x}PS$-red (x = 40, 36, and 31)

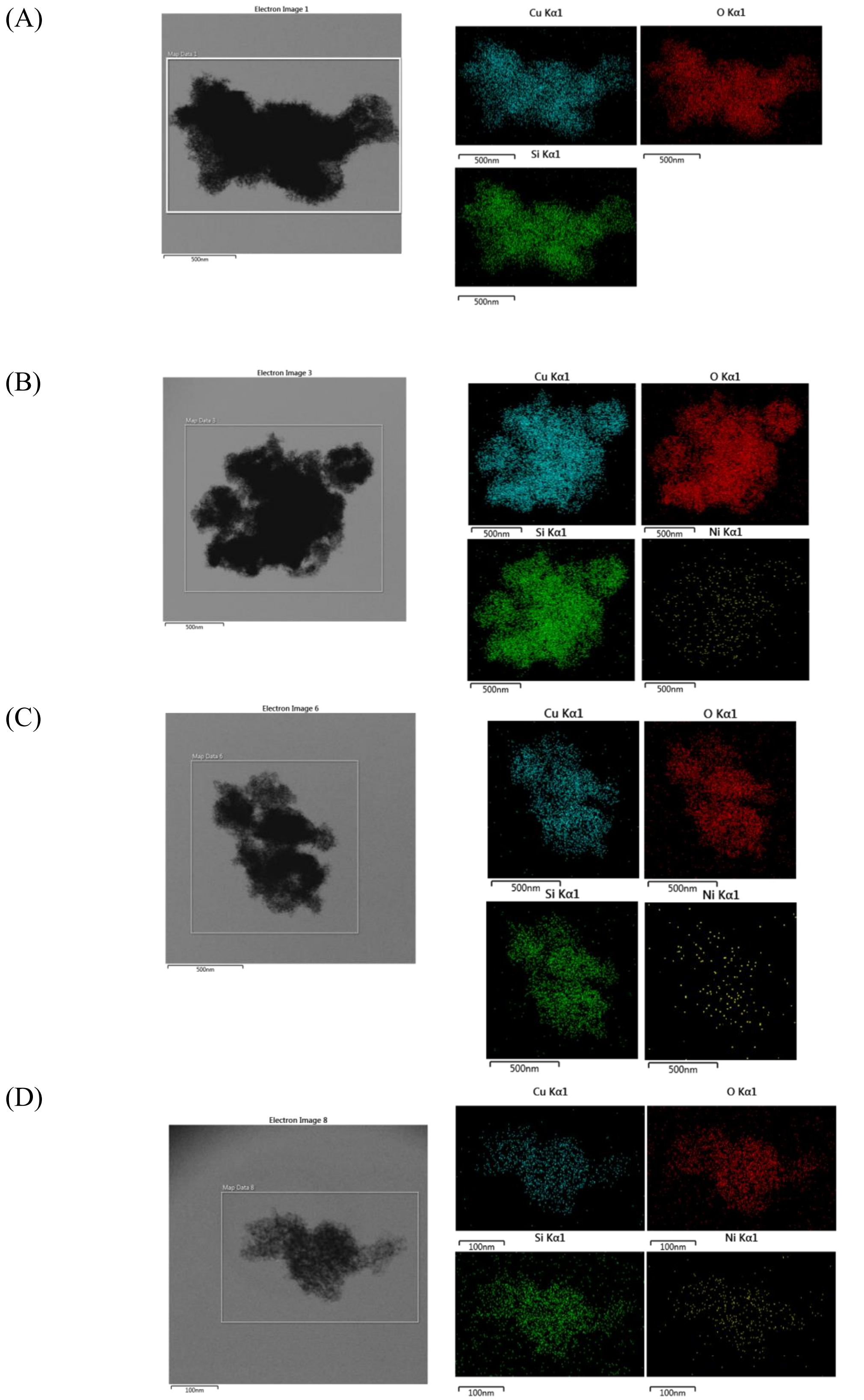


Figure S2. EDXS mapping images of Cu, O, Si, and Ni of (A) Cu_{41}PS-red, (B) $Cu_{40}Ni_{1}$PS-red-red, (C) $Cu_{36}Ni_{5}$PS-red, and (D) $Cu_{31}Ni_{10}$PS-red

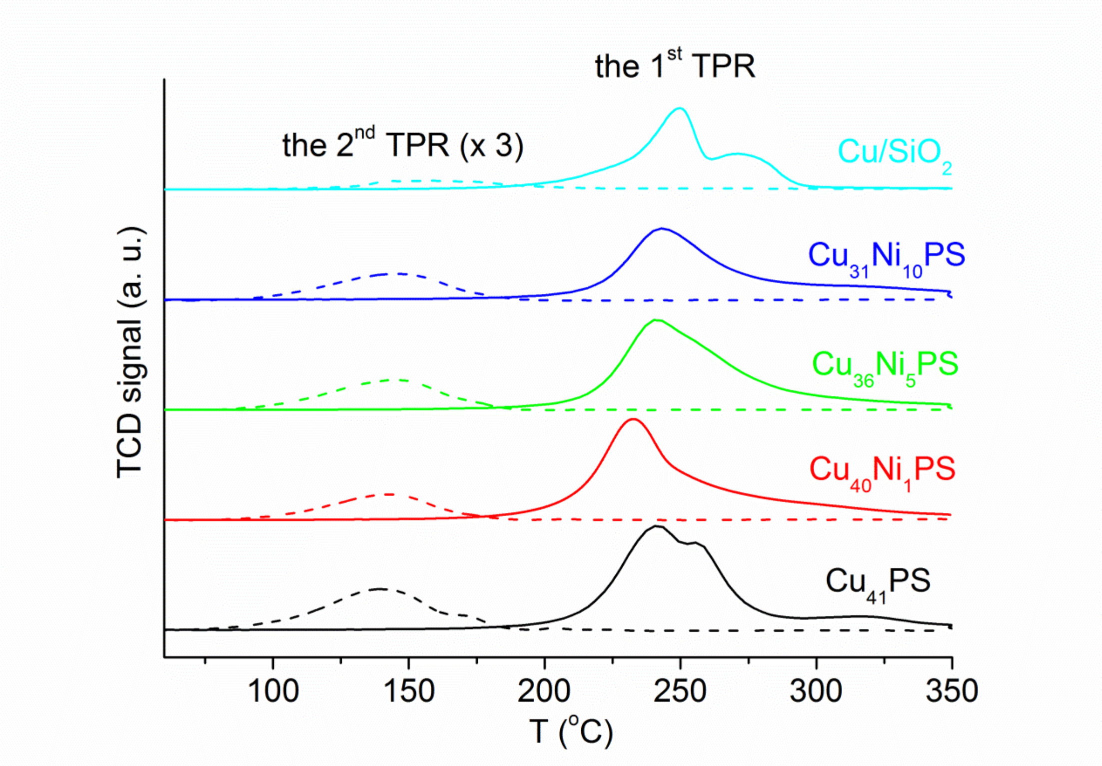


Figure S3. The first (solid line) and the second H_2-TPR profiles (dash line) after dissociative N_2O adsorption of as-prepared PS precursors and Cu/SiO_2

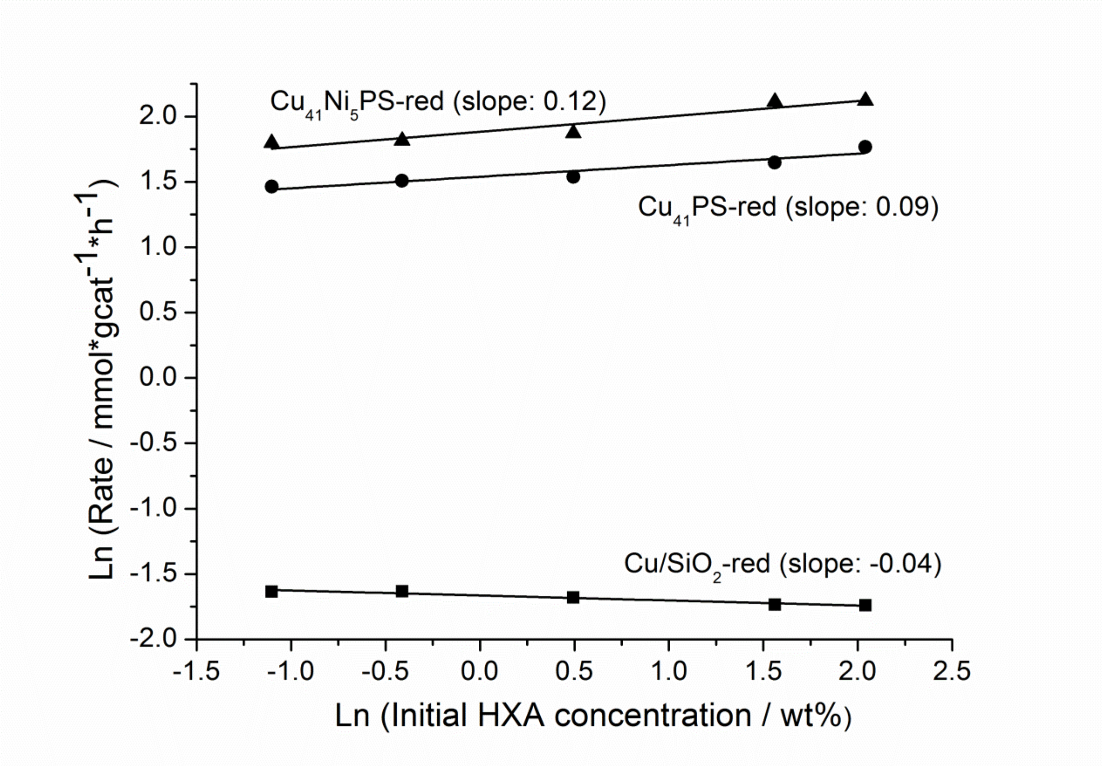


Figure S4. The log-log plot of kinetic data of hydrogenation rate with respect to initial concentration of hexanoic acid (HXA) by using Cu/SiO_2-red, Cu_{41}PS-red, and $Cu_{36}Ni_5$PS-red. Reaction conditions: HXA = 0.2, 0.4, 1.0, 2.8, or 4.6 g, 1,4-dioxane 60 mL, catalyst 0.1g, temperature 240 ºC, H_2 pressure 6 MPa, and reaction time 1 h.

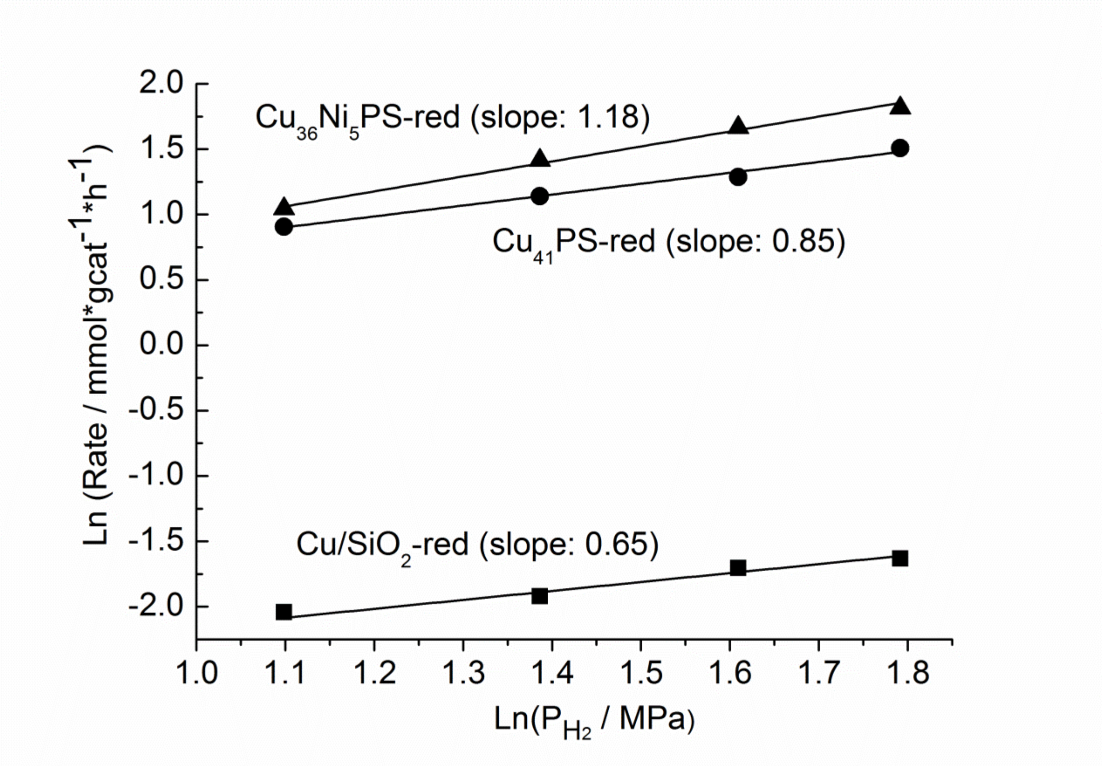


Figure S5. The log-log plot of kinetic data of hydrogenation rate of hexanoic acid (HXA) with respect to H_2 pressure by using Cu/SiO_2-red, Cu_{41}PS-red, and $Cu_{36}Ni_5$PS-red. Reaction conditions: HXA 400 mg, 1,4-dioxane 60 mL, catalyst 0.1 g, temperature 240 ºC, H_2 pressure = 3, 4, 5, or 6 MPa, and reaction time 1 h.

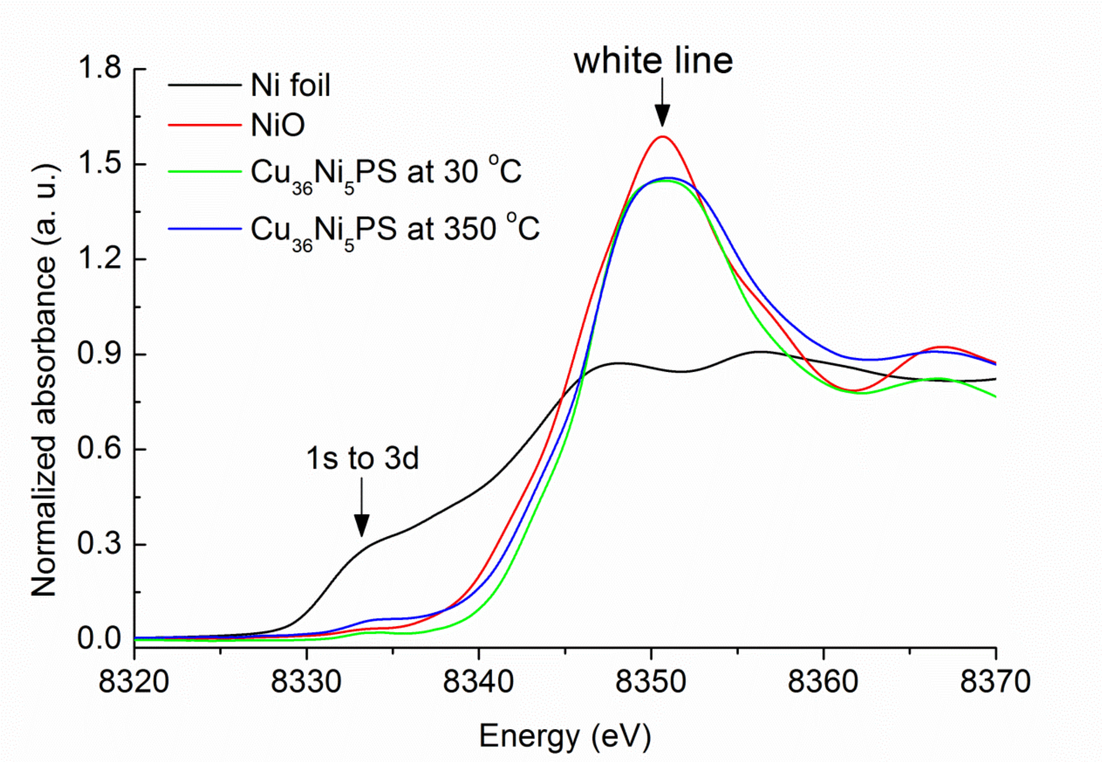


Figure S6. Ni *K*-edge XANES spectra of Ni foil, NiO, H_2-reduced $Cu_{36}Ni_5PS$ at 30 °C, and H_2-reduced $Cu_{36}Ni_5PS$ at 350 °C

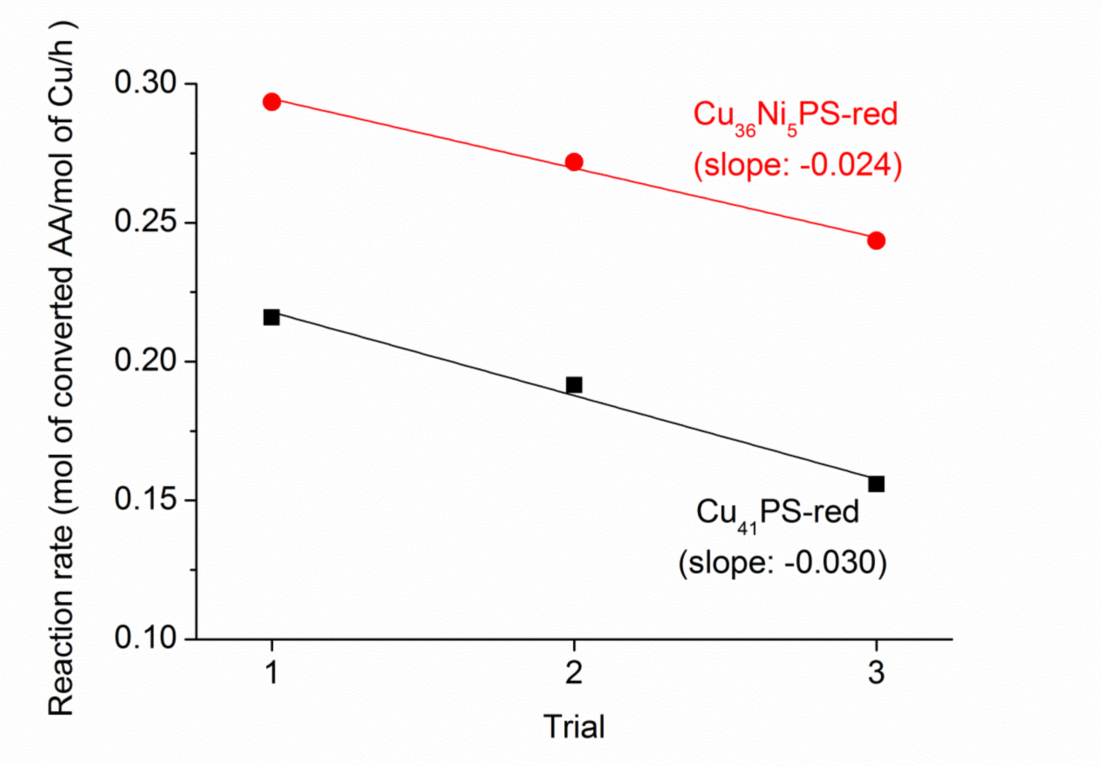
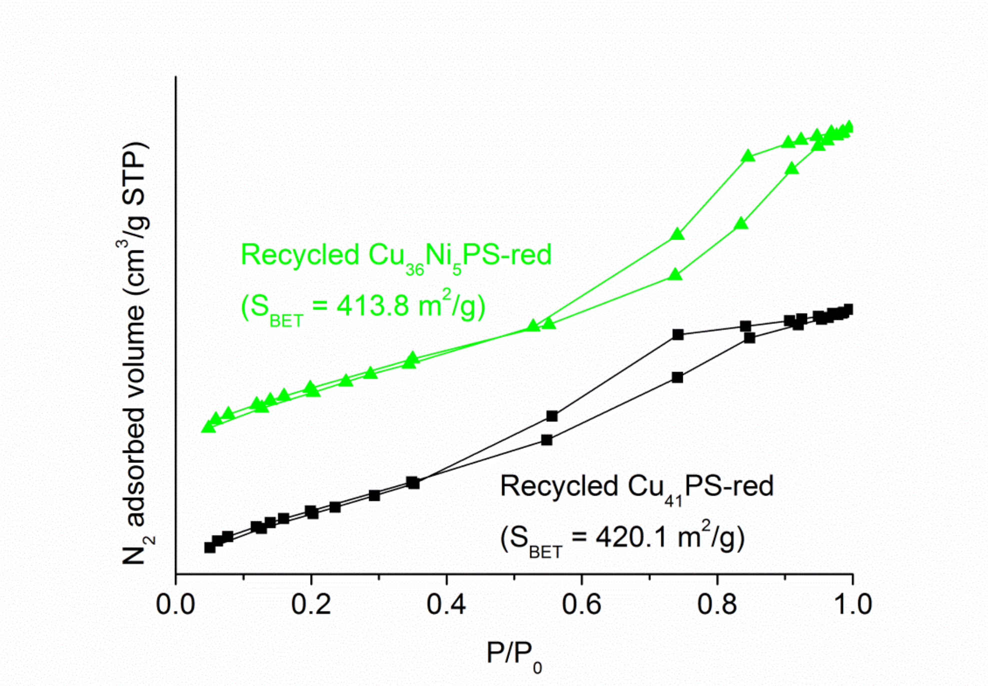


Figure S7. Deactivation rates of Cu_{41}PS-red and $Cu_{36}Ni_5$PS-red in the three consecutive trials of AA conversion

(A)



(B)

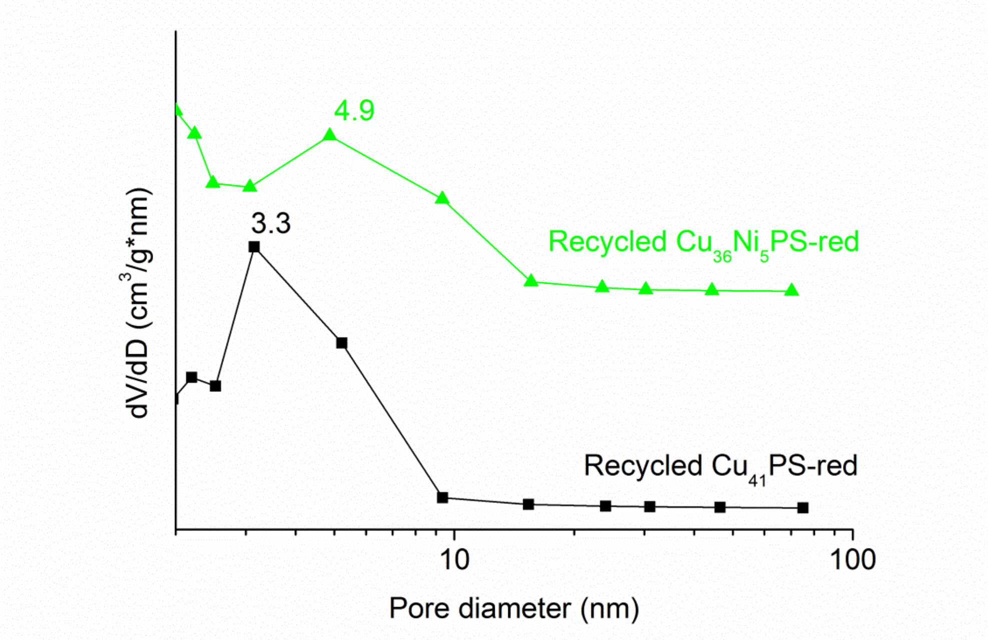


Figure S8. (A) N_2 isotherms and (B) pore size distributions of recycled Cu_{41}PS-red and $Cu_{36}Ni_5$PS-red.

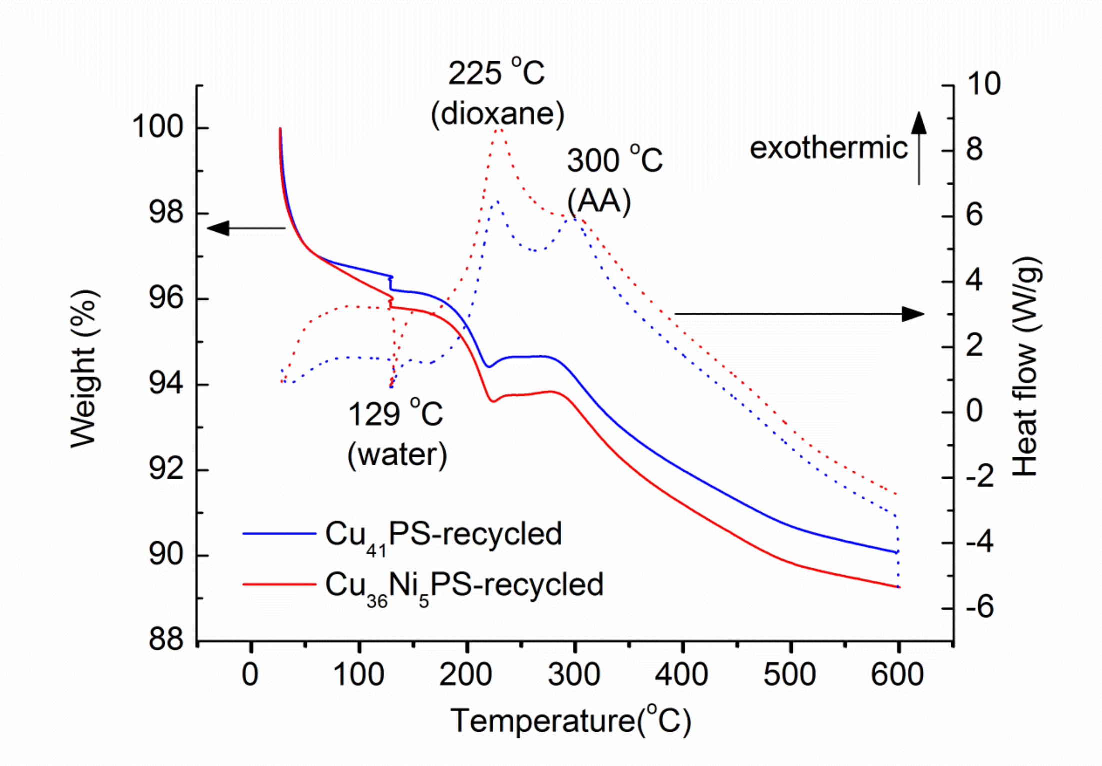
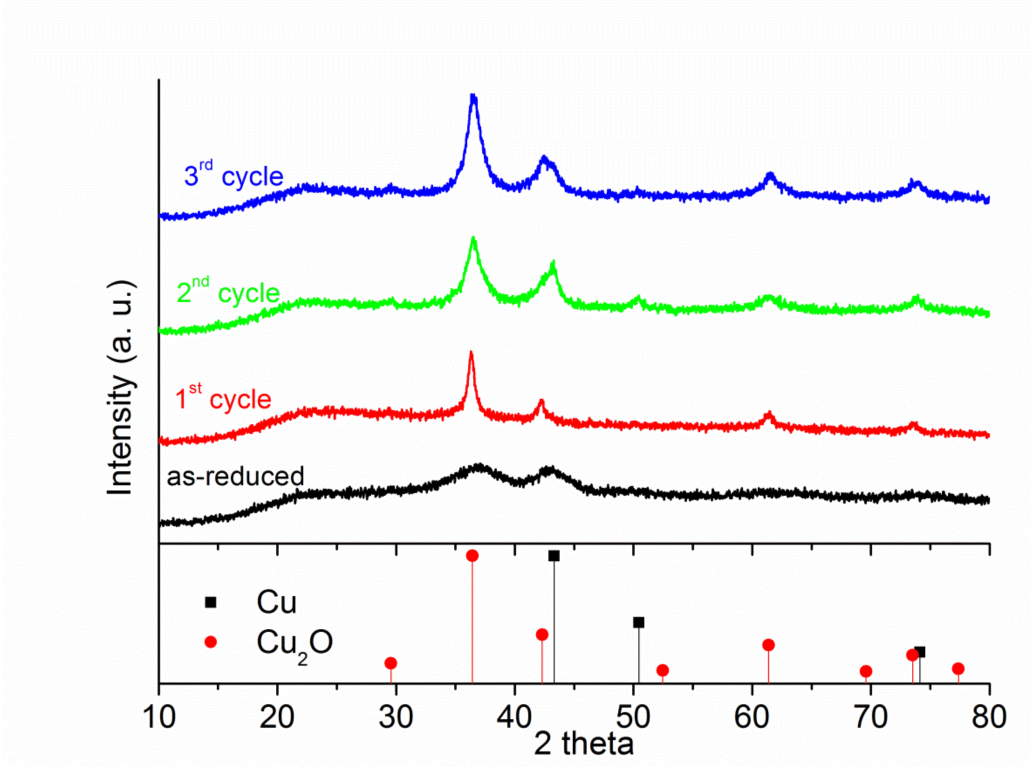


Figure S9. TGA (solid) and DTA (dash) profiles of Cu_{41}PS-red and $Cu_{36}Ni_5$PS-red after using in three successive tests in AA conversion

(A)



(B)

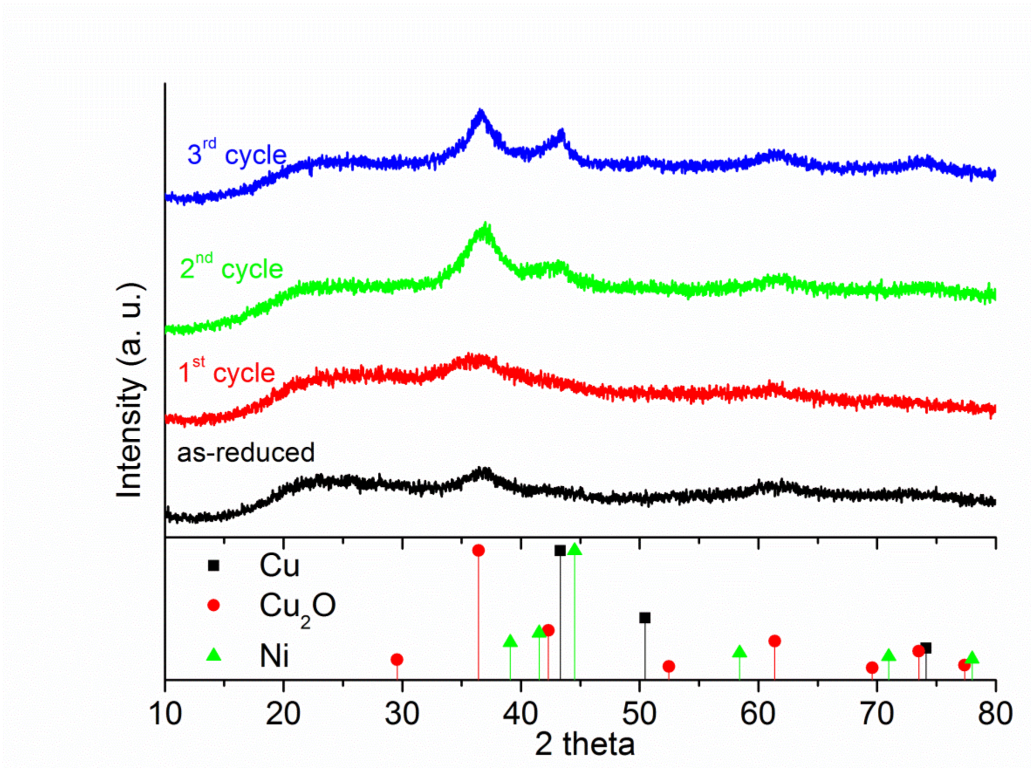


Figure S10. XRD patterns of recycled (A) Cu_{41}PS-red and (B) $Cu_{36}Ni_5$PS-red in AA hydrogenation

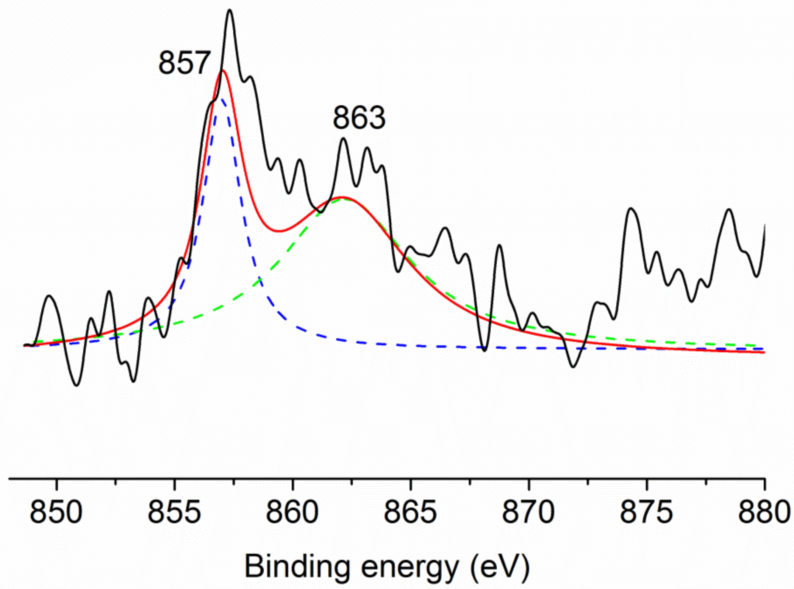


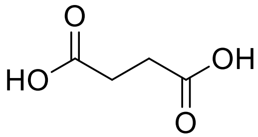
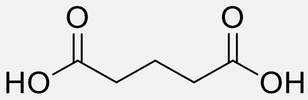
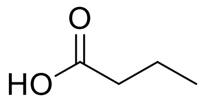
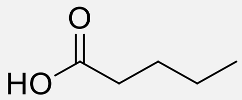
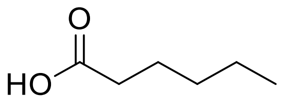
Figure S11. XPS spectrum of Ni 2p core level of recycled $Cu_{36}Ni_5PS$-red.

Table S1. Compositions and leached metals of recycled Cu_{41}PS-red and $Cu_{36}Ni_5$PS-red determined by ICP-AES analyses

	Cu_{41}PS-red		$Cu_{36}Ni_5$PS-red			
	Cu (wt%)	Leached Cu (ppm)	Cu (wt%)	Leached Cu (ppm)	Ni (wt%)	Leached Ni (ppm)
Fresh	40.4	-	35.6		3.9	
1st cycle	37.2	3.9	33.1	3.1	3.8	ND
2nd cycle	34.8	3.5	31.8	2.9	3.9	ND
3rd cycle	32.9	3.2	31.1	2.9	3.8	ND

ND = undetectable

Table S2. Initial activity of $Cu_{41}PS$-red and $Cu_{36}Ni_5PS$-red in succinic acid (SUC), glutaric acid (GLU), butyric acid (BTA), pentanoic acid (PTA) and hexanoic acid (HXA) hydrogenation to γ-butyrolactone (GBL), δ-valerolactone (DVL), n-butanol, n-pentanol and n-hexanol, respectively.[a]

	Substrate	Catalyst	X (%)	Time (h)	CB (%)	Selectivity (%)			TOF (h^{-1})
						Lactone	Diol	Mono-alcohol	
SUC		$Cu_{41}PS$-red	20.8	0.17	97.8	79.2	20.8	0	14.7
		$Cu_{36}Ni_5PS$-red	28.6	0.17	96.2	72.3	27.7	0	24.7
		Cu/SiO_2-red	25.1	3.0	86.9	78.6	21.4	0	6.5
GLU		$Cu_{41}PS$-red	24.1	0.5	96.7	82.2	17.8	0	5.1
		$Cu_{36}Ni_5PS$-red	34.1	0.5	95.4	74.4	25.6	0	9.0
		Cu/SiO_2-red	11.0	3.0	88.5	96.1	3.9	0	2.5
BTA		$Cu_{41}PS$-red	12.5	1.0	99.8	-	-	>99.9	2.0
		$Cu_{36}Ni_5PS$-red	18.8	1.0	99.9	-	-	>99.9	3.7
		Cu/SiO_2-red	1.1	6.0	90.1	-	-	>99.9	0.2
PTA		$Cu_{41}PS$-red	21.2	1.0	98.0	-	-	>99.9	2.9
		$Cu_{36}Ni_5PS$-red	28.7	1.0	97.5	-	-	>99.9	4.8
		Cu/SiO_2-red	4.3	6.0	87.0	-	-	>99.8	0.6
HXA		$Cu_{41}PS$-red	12.0	1.0	99.4	-	-	>99.9	1.4
		$Cu_{36}Ni_5PS$-red	16.3	1.0	99.8	-	-	>99.9	2.4
		Cu/SiO_2-red	3.1	6.0	86.3	-	-	>99.9	0.4

[a] Reaction condition: T = 240 ºC, P = 6 MPa