Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Online Information

Enhanced Hydrogenation of Ethyl-levulinate to γ-valerolactone over $Ni^{\delta}O_x$ Stabilized Cu^{+} surface sites

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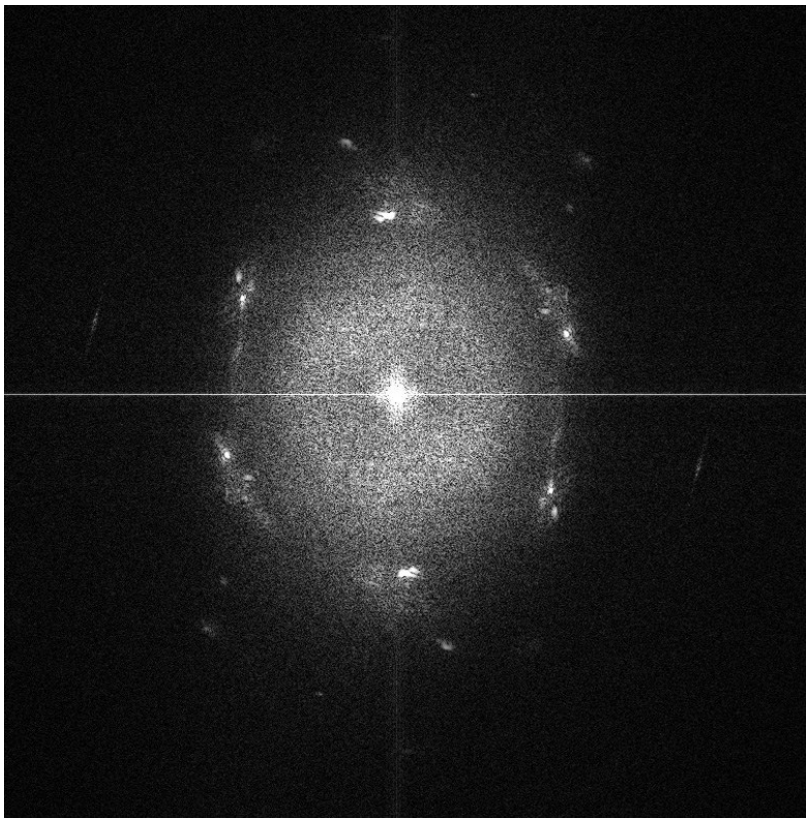


Figure.S1 *The FFT on a selected nano-particle*

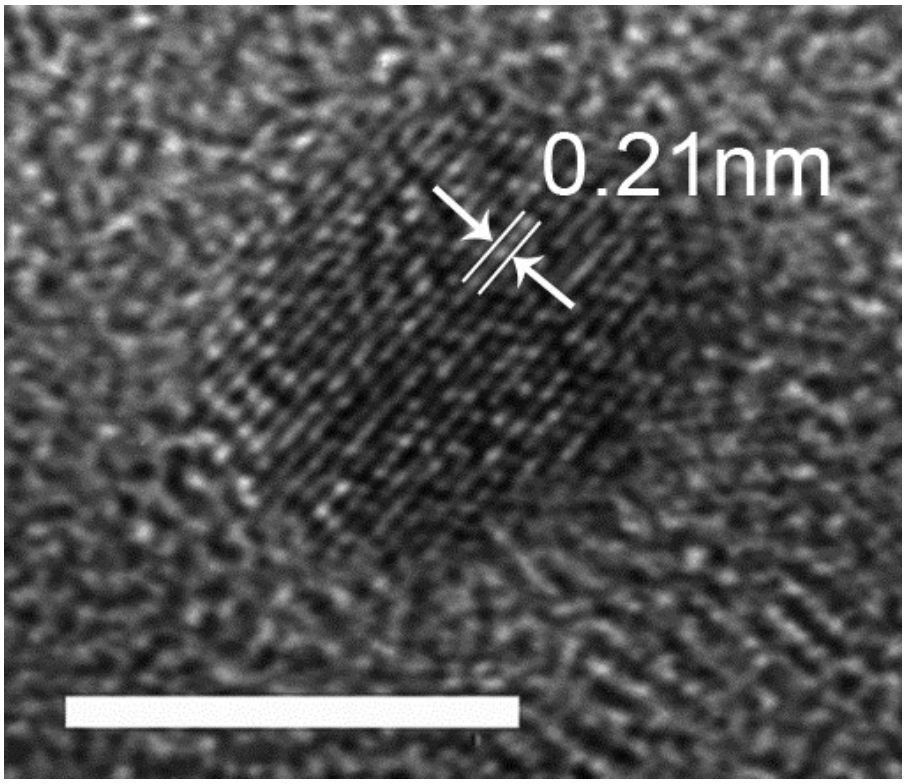


Figure.S2 HRTEM image of focused nanoparticle. The lattice with the distance of 0.21nm corresponds to Cu (111) planes . The scaled bar is 2nm.

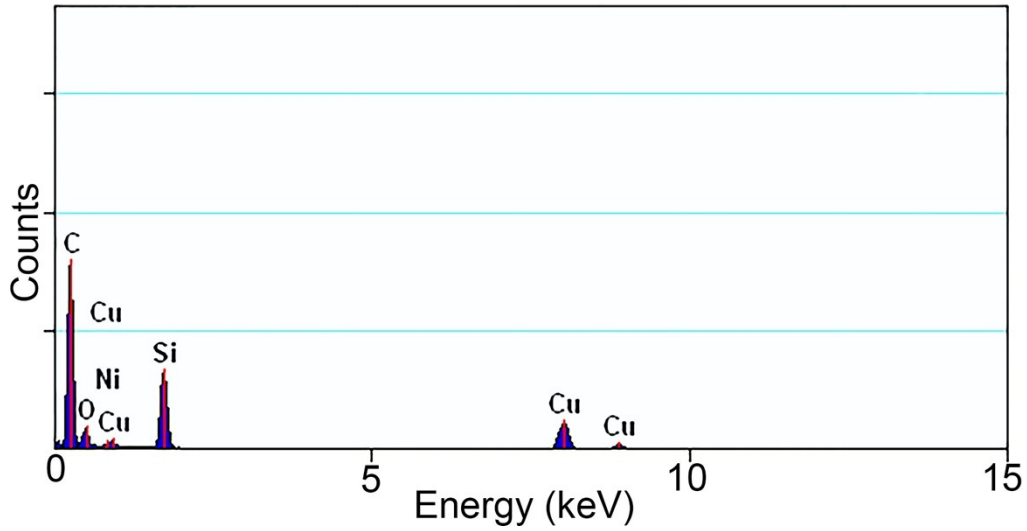


Figure.S3 EDS result on a nano-cluster of Cu(35%)Ni(4%)/SiO_2 catalyst

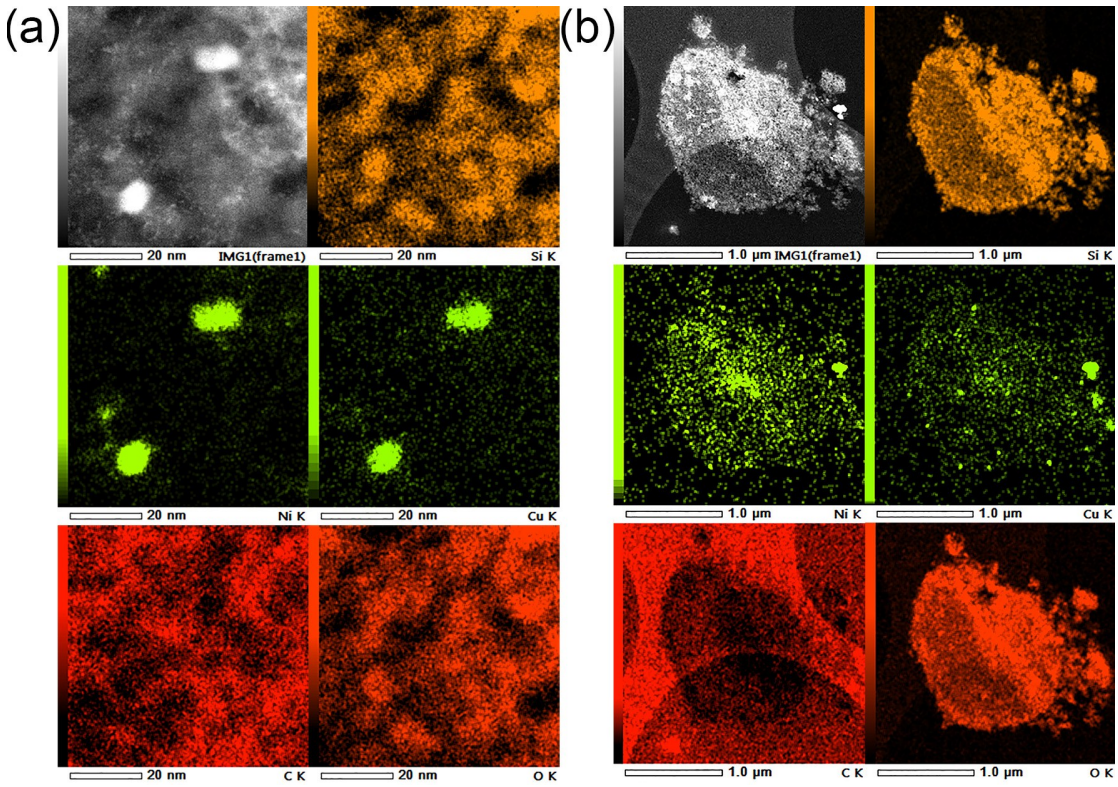


Figure.S4 EDS mappings on (a) 20nm scale and (b)1000nm scale. Each figure Includes HAADF image, Si, Ni, Cu, C and O co

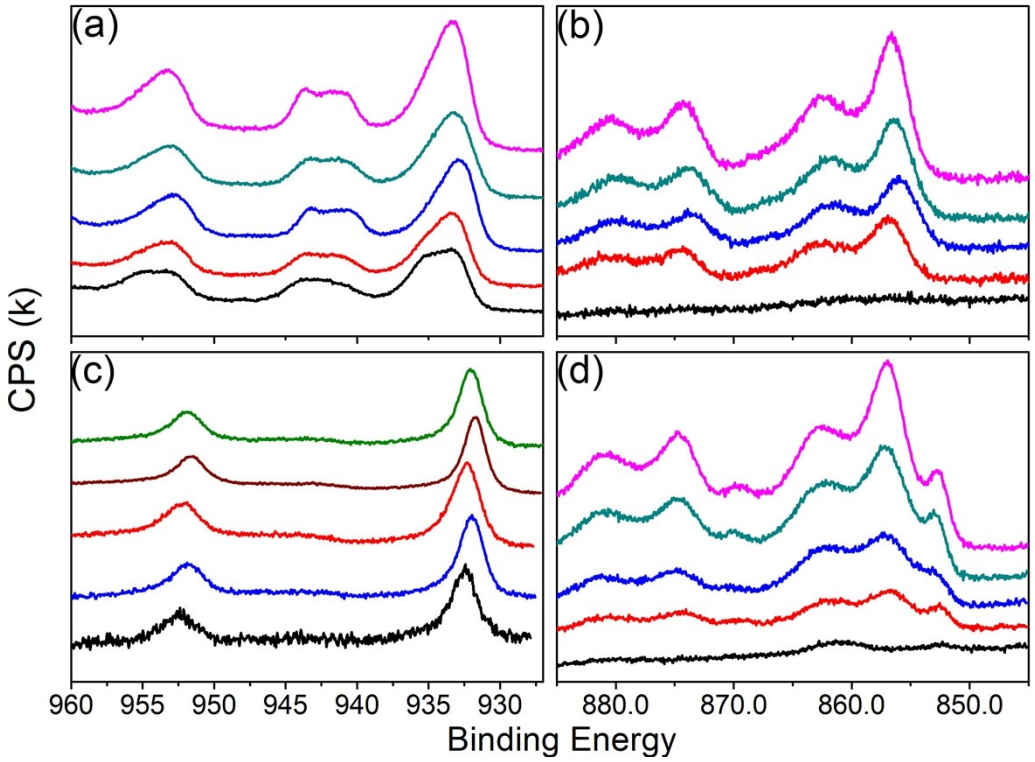


Figure.S5 Cu2p XPS diagram of (a) before and (c) after reduction; Ni2p3/2 XPS diagram of (b) before and (d) after reduction. Seen from (a) and (b), the copper and nickel has fully Cu^{2+} and Ni^{2+}, respectively. (c) After reduction by H_2, Cu^{2+} was reduced completely. To deffer Cu^{+} or Cu^{0} remained, auger electronic spectrom (AES) was carried out to detect the state of reduced copper. See the AES result on Figure S4 and Table S1. (d) There has much Ni^{2+} remained even after reduction. One new peak occurred at about 853eV, implying the Ni^{2+} was partly reduced. Comparing to the standard Ni^{0} of 852.3eV. The nickel possessed a state of ($0 \le \delta < 2$). Series of $CuNi/SiO_2$ catalysts with different Ni content were showed as different color. black line: Ni(0%), red line: Ni(2%), blue line: Ni(4%), green line: Ni(6%), pink line: Ni(8%). See direct numeral data of Ni2p3/2 XPS on table S2.

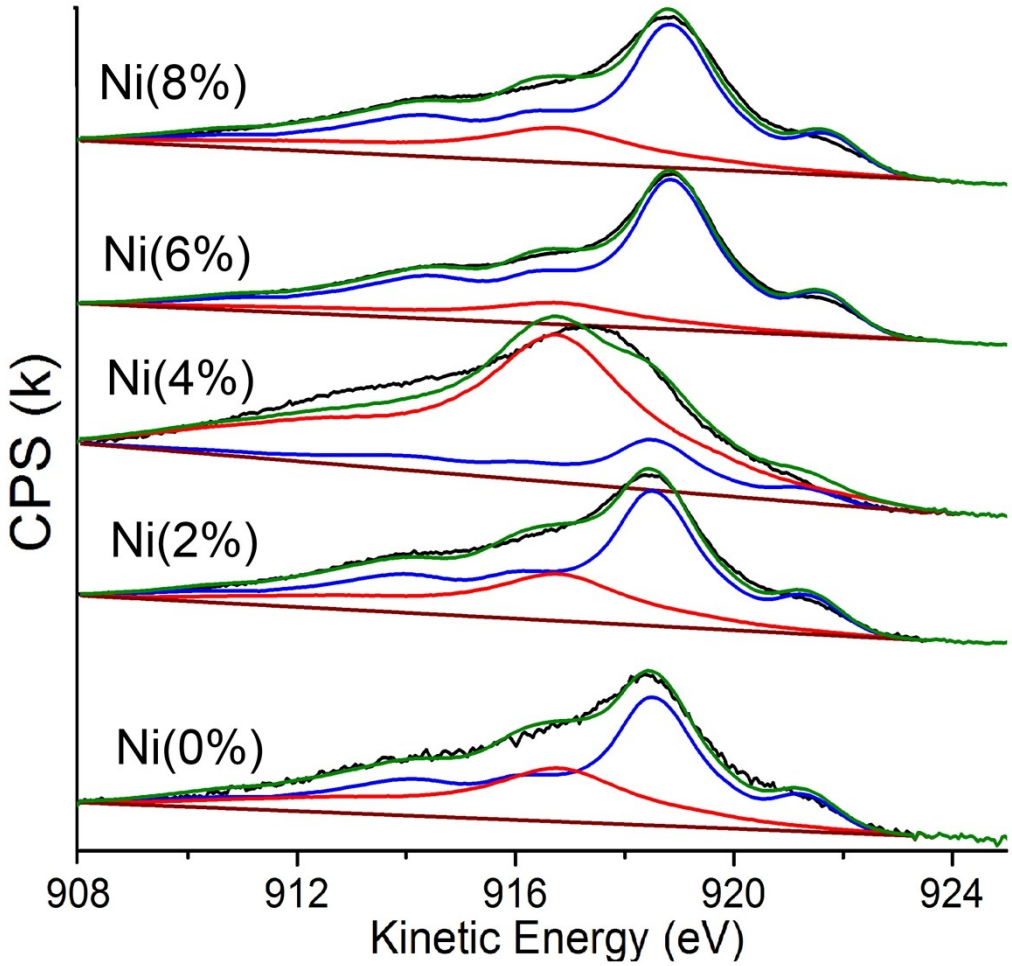


Figure.S6 The Cu 2p AES diagrams with different Ni content after reduction. Brown line: base; red line: Cu^{+}; blue line: Cu^{0}; green line: envelope; black line: real cps.

Table S1 The Cu LMM XAES result of catalysts with different Ni content after reduction

Catalyst	KE（eV）		α'（eV）		X_{Cu^+}[a] %	X_{Cu^0}[a] %
	Cu^+	Cu^0	Cu^+	Cu^0		
Cu-Ni(0%)/SiO_2	916.0	918.7	1848.4	1850.8	28.35	71.65
Cu-Ni(2%)/SiO_2	915.6	918.3	1848.3	1851.0	33.46	66.54
Cu-Ni(4%)/SiO_2	915.7	918.5	1848.0	1850.8	79.19	20.81
Cu-Ni(6%)/SiO_2	915.7	918.4	1848.3	1851.0	23.33	76.67
Cu-Ni(8%)/SiO_2	915.5	918.5	1848.3	1851.3	15.06	84.94

a：Intensity ratio of Cu^+(or Cu^0)/(Cu^++Cu^0) by deconvolution of Cu LMM XAES spectra

Table S2 The Ni 2p3/2 binding energy of catalysts with different Ni content before and after reduction

Catalyst	before reduction	after reduction	
	Ni 2p3/2, eV	**Ni 2p3/2, eV**	**Ni 2p3/2, eV**
Cu-Ni(0)/SiO_2	-	-	-
Cu-Ni(2%)/SiO_2	856.7	856.9	852.6
Cu-Ni(4%)/SiO_2	855.8	857.4	853.2
Cu-Ni(6%)/SiO_2	856.5	857.0	853.0
Cu-Ni(8%)/SiO_2	856.7	856.9	852.8
NiO[a]	853.3	-	-
Ni[a]	-	-	852.3

a：the binding energy data of NiO and Ni referring to the handbook of XPS

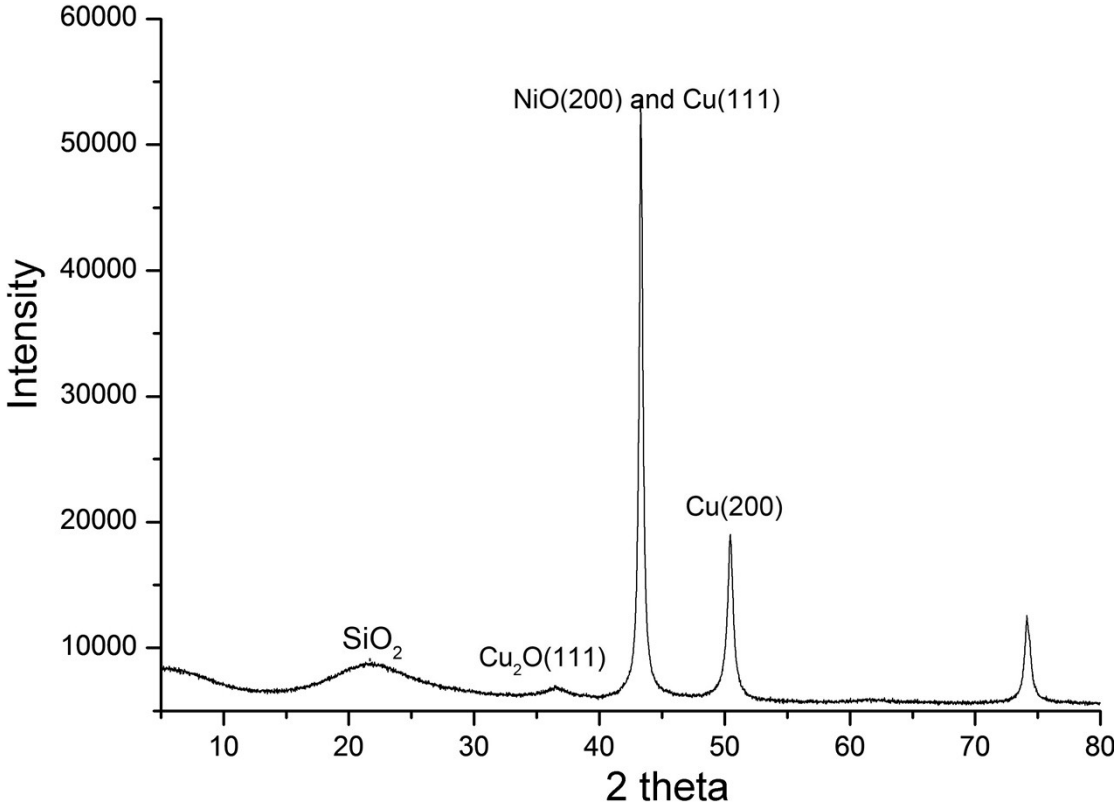
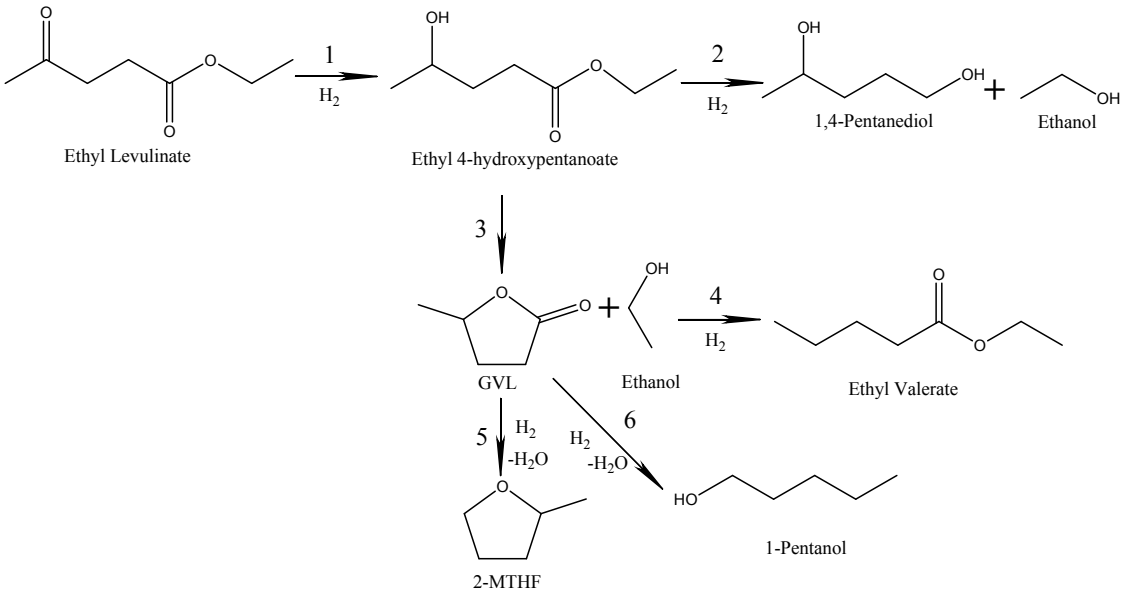


Figure.S7 XRD curve of $CuNi^{\delta}O_x/SiO_2$ catalyst after 200 hours' reaction.



Scheme S1. The proposed reaction pathways of EL hydrogenation.