

Electronic Supplementary Material

Enhanced synergy between Cu⁰ and Cu⁺ on nickel doped copper catalyst for gaseous acetic acid hydrogenation

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The conversion of acetic acid and selectivity were calculated by equation 1 and 2, respectively.

The STY (space time yield) of ethanol was calculated as hourly produced ethanol on per gram catalyst (equation 3) at the conditions of T = 300°C, P = 2.7 MPa and H₂/AA = 20 (mol / mol) .

$$\text{conversion} = \frac{\text{mol of HAC put into reactor} - \text{mol of HAC remaian in product}}{\text{mol of HAC put into reactor}} \quad \text{equation 1}$$

$$\text{selectivity} = \frac{\text{mol of HAC consumed to ethanol or ethyl acetate}}{\text{mol of HAC put into reactor} - \text{mol of HAC remaian in product}} \quad \text{equation 2}$$

$$\text{STY} = \frac{F_{\text{HAC}} \times \rho_{\text{HAC}} \div \text{MW}_{\text{HAC}} \times \text{Conv.} \times \text{Sel}_{\text{EtOH}} \times \text{MW}_{\text{EtOH}}}{m_{\text{cat}}} \quad \text{equation 3}$$

F_{HAC} : flow rate of HAC (mL/h)

ρ_{HAC} : density of HAC (g/mL)

MW_{HAC} : the relative mass of HAC (g/mol)

Conv. : the conversion of HAC (%)

Sel_{EtOH} : the selectivity of EtOH (%)

MW_{ETOH} : the relative mass of ETOH (g/mol)

m_{cat} : the mass of catalyst filled in the reactor (g)

Table S1 Integral quantity of hydrogen consumption of various catalysts

Catalysts	Peak 1			Peak 2		
	T1 /°C	Area /%	H ₂ consumption /mL·g _{cat} ⁻¹	T2 /°C	Area /%	H ₂ consumption /mL·g _{cat} ⁻¹
Cu/SiO ₂ - AE	182	40.58	22.9	221	59.41	33.5
Cu/SiO ₂ - 0.3Ni	183	33.48	19.9	239	66.51	39.7
Cu/SiO ₂ - 0.5Ni	180	27.11	17.3	225	72.88	46.6
Cu/SiO ₂ - 1 Ni	193	24.56	15.7	234	75.42	48.2
Cu/SiO ₂ - 1.5Ni	196	20.12	12.8	230	79.85	51.0

Table S2 Catalytic performance of the various catalysts

Catalysts	WHSV = 1.5 h ⁻¹					WHSV = 2 h ⁻¹			
	Conv. /%	S _{EtOH} /%	S _{AcOEt} /%	S _{ether} /%	S _{Alde} /%	Conv. /%	S _{EtOH} /%	S _{AcOEt} /%	S _{Alde} /%
Cu/SiO ₂ - AE	99.49	91.05	4.91	0.25	1.89	88.9	57.1	41.7	1.2
Cu/SiO ₂ - 0.3Ni	99.65	89.98	4.03	5.32	0.43	95.9	65.6	32.5	1.6
Cu/SiO ₂ - 0.5Ni	99.90	90.67	2.97	6.22	0.21	97.9	70.1	26.7	2.1
Cu/SiO ₂ - 1.5Ni	99.42	90.17	4.71	4.05	0.31	96.8	66.6	30.5	1.8
Cu/SiO ₂ - 3Ni	96.79	84.89	11.82	3.71	1.02	79.4	55.4	42.5	1.3

Reaction conditions: T=573 K, P=2.7 MPa, H₂/AA=20

Table S3 Metal dispersion and surface area of different copper species on various reduced catalysts

Catalysts	D ^a	S _{Cu0} ^a	S _{Cu+}	X _{Cu+}
	/%	/m ² • g ⁻¹	/m ² • g ⁻¹	/%
Cu/SiO ₂ - AE	39	50.6	29.4	38.9
Cu/SiO ₂ - 0.3Ni	35	46.2	32.8	41.5
Cu/SiO ₂ - 0.5Ni	26	34.3	33.3	48.5
Cu/SiO ₂ - 1.5Ni	22	31.2	23.6	43.1
Cu/SiO ₂ - 3Ni	20	29.9	19.6	37.4

^a Dispersion and surface area of metallic copper on reduced catalysts calculated from N₂O titration results

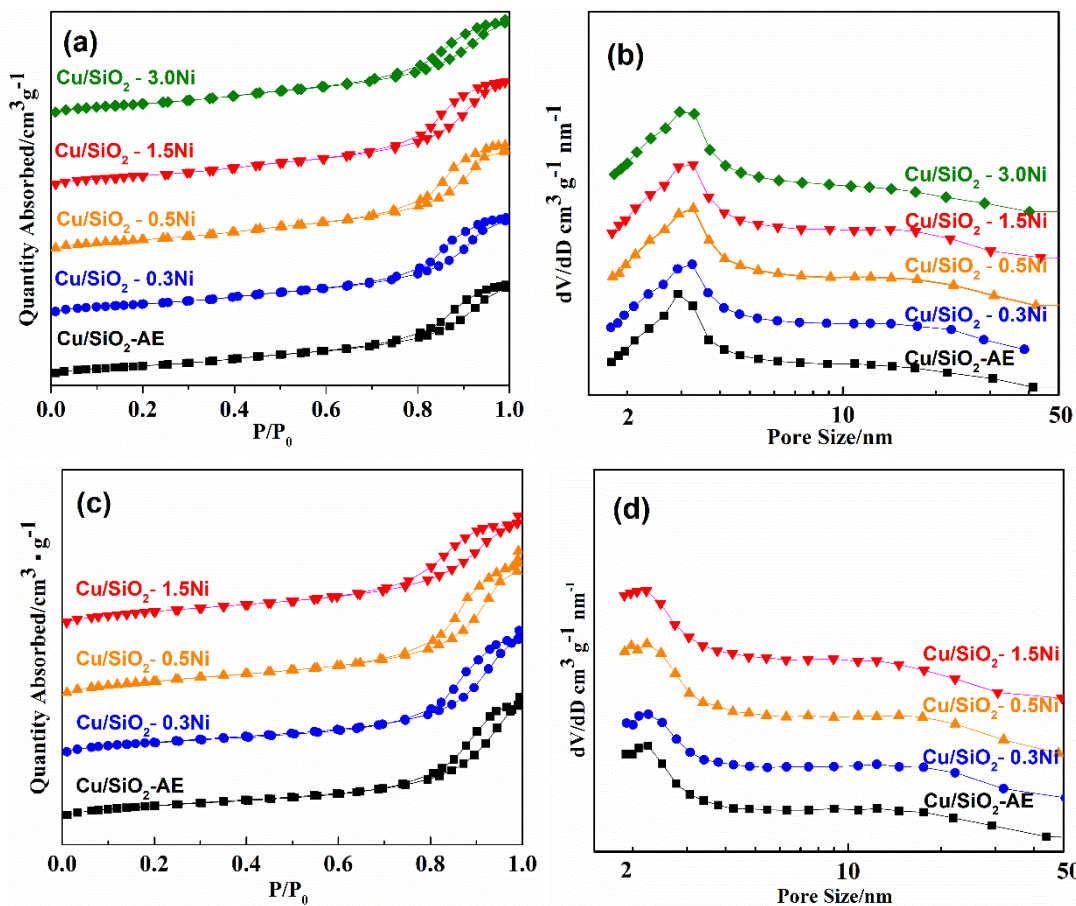


Fig. S1. N_2 adsorption-desorption curves of reduced catalysts (a) and used catalysts (c) and pore size distribution of reduced catalysts (b) and used catalysts (d)

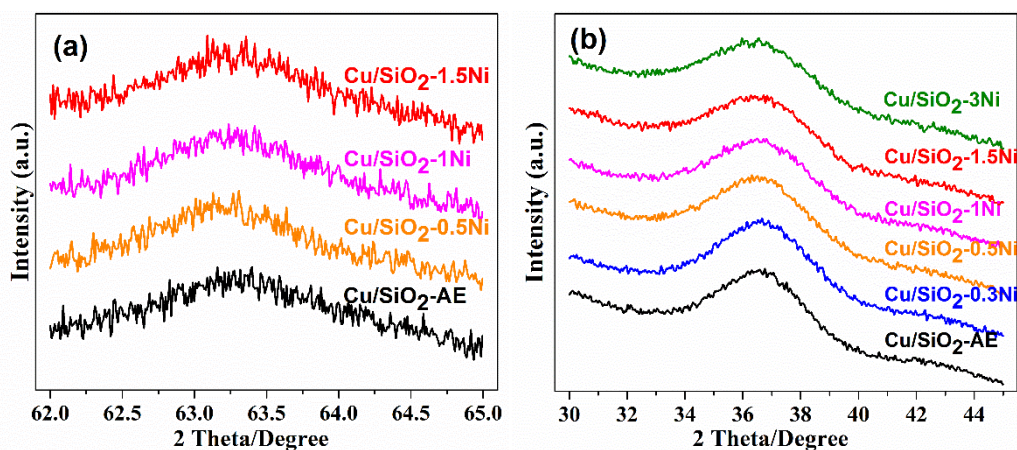


Fig. S2 Regional XRD patterns of calcined (a) and reduced (b) catalysts.

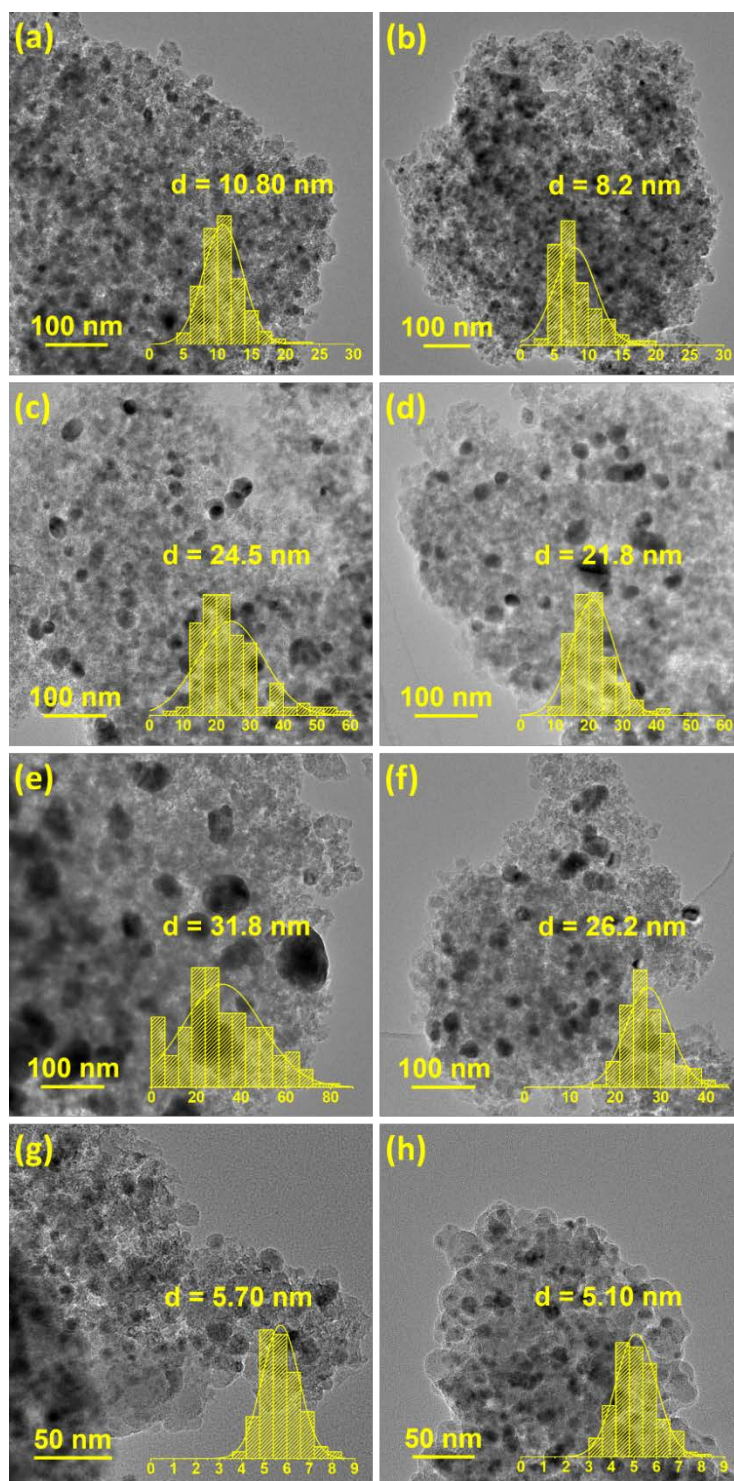


Fig. S3 HRTEM images of catalysts treated by different treatment methods

- (a) $\text{H}_2\text{O} + \text{N}_2\text{-Cu/SiO}_2\text{-AE}$, (b) $\text{H}_2\text{O} + \text{N}_2\text{-Cu/SiO}_2\text{-0.5Ni}$,
(c) $\text{HAC} + \text{N}_2\text{-Cu/SiO}_2\text{-AE}$, (d) $\text{HAC} + \text{N}_2\text{-Cu/SiO}_2\text{-0.5Ni}$,
(e) $\text{HAC} + \text{H}_2\text{O} + \text{N}_2\text{-Cu/SiO}_2\text{-AE}$, (f) $\text{HAC} + \text{H}_2\text{O} + \text{N}_2\text{-Cu/SiO}_2\text{-0.5Ni}$,
(g) $\text{H}_2 + \text{H}_2\text{O-Cu/SiO}_2\text{-AE}$, (h) $\text{H}_2 + \text{H}_2\text{O-Cu/SiO}_2\text{-0.5Ni}$,