Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Copper-based catalysts with tunable acidic and basic sites for the selective conversion of levulinic acid/ester to γ-valerolactone or 1,4-pentanediol

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Table S1 Reduction degree and elemental compositions of Cu-based catalysts

Entry	Catalysts	Reduction degree (%)[a]	Elemental compositions[b] (wt %)			Fraction[c] (%)	
			Cu	Mg	Al	Cu^{2+}	Cu^{+}+Cu^{0}
1	CuAl-fresh	86.4	72.3	−	11.1	72.1	27.9
2	CuAl-used	−	73.7	−	9.5	75.0	25.0
3	CuMgAl-1-4-fresh	74.3	18.7	26.2	13.0	−	−
4	CuMgAl-1-2-fresh	82.6	25.1	21.5	11.9	−	−
5	CuMgAl-1-1-fresh	72.9	43.7	15.1	11.1	74.8	25.2
6	CuMgAl-1-1-used	−	43.3	14.1	9.8	76.3	23.7
7	CuMg-fresh	94.6	42.0	27.3	−	−	−
8	CuMg-used	−	45.1	23.7	−	−	−

[a]It represents the reduction degree of calcined Cu-based catalysts.

[b]Elemental compositions are measured by EDX.

[c]The fraction of different Cu states is calculated based on XPS results.

Table S2 Distribution of the products in hydrogenation of LA in different solvents[a]

Entry	Solvents	Catalysts	Con. (%)	Yield (%)	
				GVL	1,4-PDO
1	Ethanol	CuMgAl-1-4	100.0	68.7	15.8
2	Ethanol	CuMgAl-1-2	100.0	70.2	19.4
3	Ethanol	CuMgAl-1-1	100.0	63.8	22.1
4	Isopropanol	CuMgAl-1-4	100.0	54.6	38.1
5	Isopropanol	CuMgAl-1-2	100.0	29.0	62.7
6	Isopropanol	CuMgAl-1-1	100.0	31.9	56.1

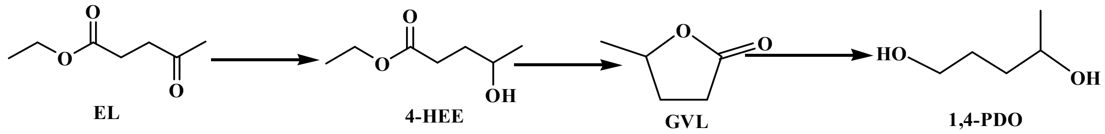
[a]Reaction conditions: temperature = 170°C; t = 2 h; P_{H2} = 3 MPa (at room temperature); stirring speed = 400 rpm; catalyst loading: 40 mg; reactant loading: 40 mg; solvent: 3.96 g.

Table S3 Distribution of the products in hydrogenation of LA and EL in isopropanol[a]

Entry	Substrates	Catalysts	Con. (%)	Yield (%)	
				GVL	1,4-PDO
1	LA	CuMgAl-1-4	100.0	54.6	38.1
2		CuMgAl-1-2	100.0	29.0	62.7
3		CuMgAl-1-1	100.0	31.9	56.1
4	EL	CuMgAl-1-4	100.0	36.0	58.0
5		CuMgAl-1-2	100.0	15.1	83.2
6		CuMgAl-1-1	100.0	25.1	72.5

[a]Reaction conditions: temperature = 170°C; t = 2 h; P_{H2} = 3 MPa (at room temperature); stirring speed = 400 rpm; catalyst loading: 40 mg; reactant loading: 40 mg; isopropanol: 3.96 g.

Table S4 Distribution of the products in hydrogenation of EL in isopropanol[a]



Entry	P_{H2} (MPa)	Catalysts	Con. (%)	Yield (%)	
				GVL	1,4-PDO
1	6.0	CuMgAl-1-1-300[b]	100.0	4.7	94.5
2	6.0	CuMg-300	100.0	6.6	92.6
3	6.0	CuMgAl-1-1-400	100.0	5.6	93.9
4	6.0	CuMg-400	100.0	4.1	94.7
5	6.0	CuMg-300-400	100.0	7.7	91.4

[a]Reaction conditions: t = 3 h; T = 140°C; stirring speed = 400 rpm; catalyst loading: 40 mg; reactant loading: 40 mg; isopropanol: 3.96 g.

[b]CuMgAl-1-1-300 and CuMg-300 represent that the reduced catalyst was reduced at 300°C for 2 h again. CuMgAl-1-1-400 and CuMg-400 represent that the reduced catalyst was reduced at 400°C for 2 h again. CuMg-300-400 represents that the reduced catalyst was reduced at 300°C for 2 h and then reduced at 400°C for 2 h.

Table S5 Particle size of fresh Cu-based catalysts

Entry	Catalysts	Cu particle size (nm)
1	CuMgAl-1-1-300[a]	6.6
2	CuMg-300	10.1
3	CuMgAl-1-1-400	6.5
4	CuMg-400	9.6
5	CuMg-300-400	11.2

[a]CuMgAl-1-1-300 and CuMg-300 represent that the reduced catalyst was reduced at 300°C for 2 h again. CuMgAl-1-1-400 and CuMg-400 represent that the reduced catalyst was reduced at 400°C for 2 h again. CuMg-300-400 represents that the reduced catalyst was reduced at 300°C for 2 h and then reduced at 400°C for 2 h.

Table S6 Distribution of the products in hydrogenation of levulinic acid/ester into GVL or 1,4-PDO

Reactant	Catalysts	Reaction conditions	Con. (%)	Yield (%)	Ref.
LA	Pt-Mo/HAP	T = 130°C; t = 24 h; H_2 = 3 MPa; Solvent = water	100.0	1,4-PDO 93.0	[10]
LA	Pd-Cu/ZrO_2	T = 200°C; t = 24 h; H_2 = 6 MPa; solvent = water	100.0	GVL 100.0	[48]
LA	Ni/Al_2O_3	T = 200°C; t = 4 h; H_2 = 5 MPa; solvent = H_2O	100.0	GVL 92.0	[49]
LA	NiCuMgAlFe	T = 142°C; t = 3 h; H_2 = 2 MPa; solvent = methanol	100.0	GVL 98.1	[50]
LA	Ni/$Mg_2Al_2O_5$	T = 160°C; t = 1 h; H_2 = 2 MPa; solvent = methanol	100.0	GVL 99.7	[51]
GVL	CuMgAlO	T = 160°C; t = 12 h; H_2 = 5 MPa; 1,4-dioxane	93.0	1,4-PDO 99	[28]
EL	CuMg	T = 140°C; t = 6 h; H_2 = 6 MPa; solvent = isopropanol	>99	1,4-PDO >99	In this study
EL	CuMgAl-1-1	T = 140°C; t = 6 h; H_2 = 6 MPa; solvent = isopropanol	>99	1,4-PDO >99	In this study
LA	CuAl	T = 110°C; t = 2 h; H_2 = 3 MPa; solvent: ethanol	>99	GVL 95.3	In this study

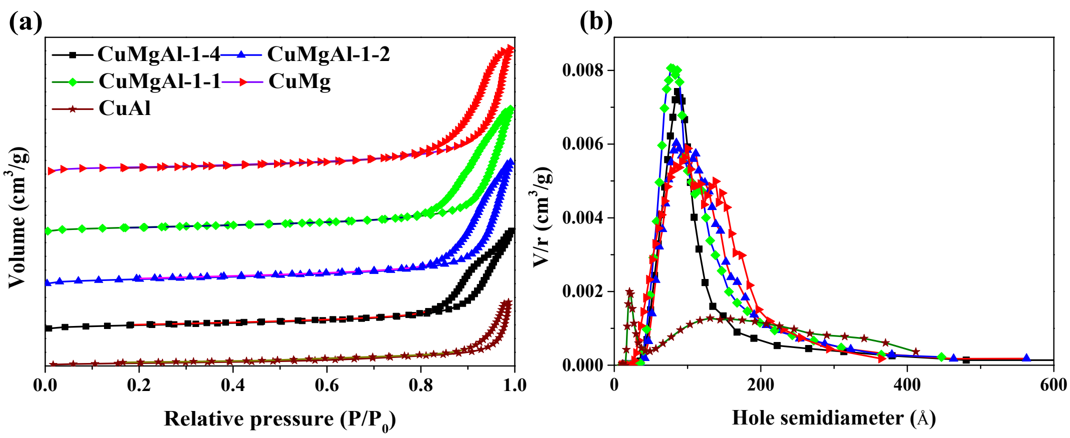


Fig. S1 The isothermal curves and pore distribution diagram of BJH desorption hole for Cu based catalysts before reduction.

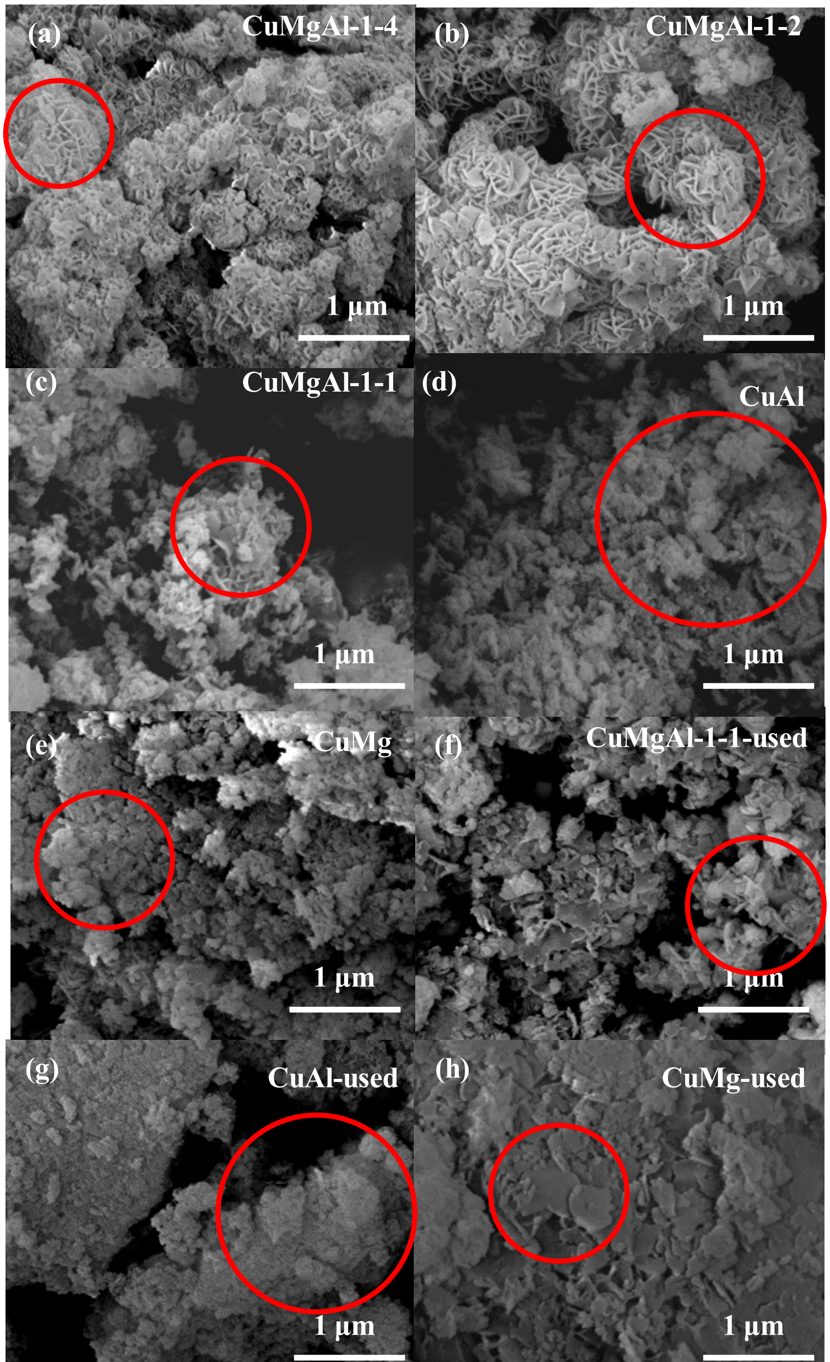


Fig. S2 SEM images of (a) to (e): fresh CuMgAl, CuAl and CuMg catalysts; and: (f) to (h): used CuMgAl-1-1, CuAl and CuMg catalysts.

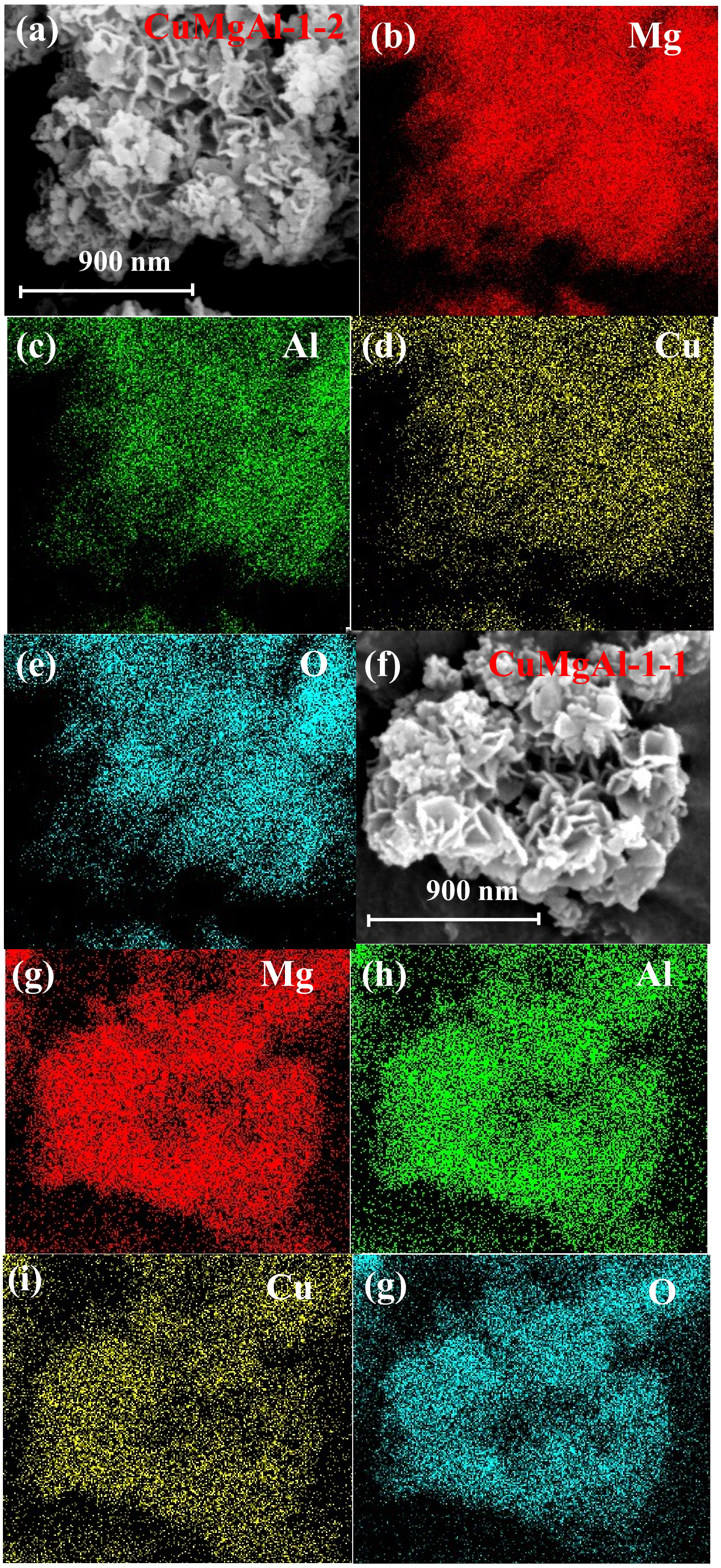


Fig. S3 SEM image of CuMgAl-1-2 and CuMgAl-1-1 catalysts and the corresponding elemental mappings of Mg, Al, Cu and O. (a) to (e): CuMgAl-1-2 catalyst and elemental mapping; (f) to (g): CuMgAl-1-1 catalyst and elemental mapping.

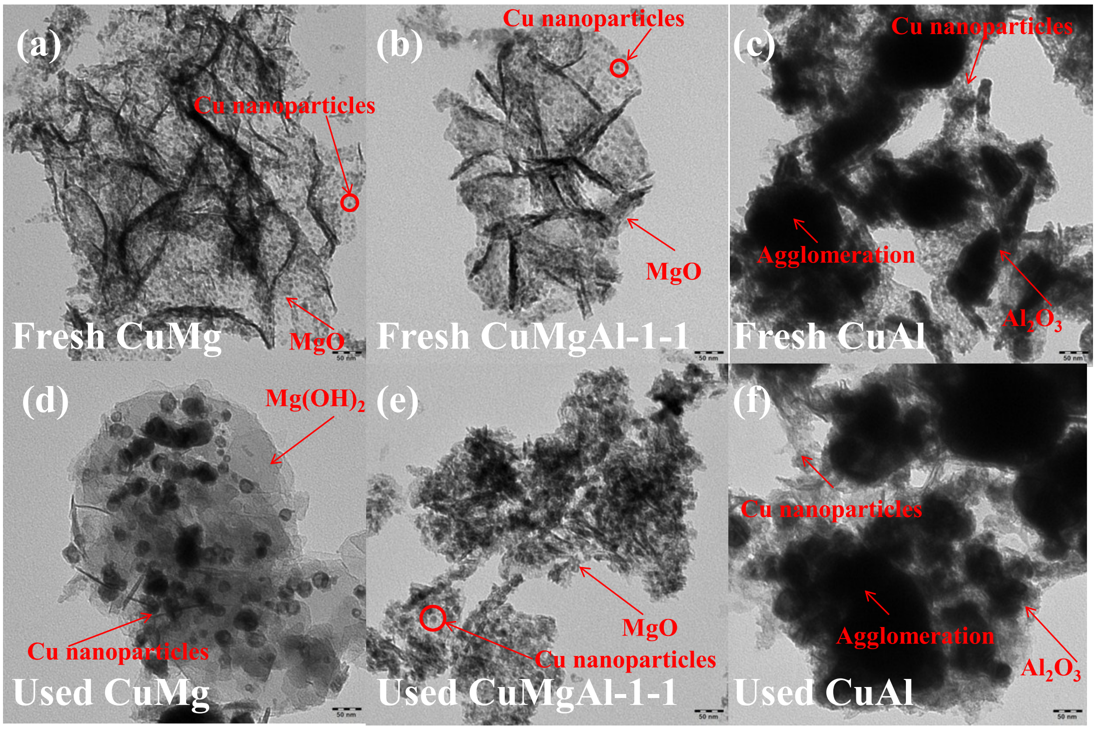


Fig. S4 TEM images of (a) to (c) fresh CuMg, CuMgAl-1-1 and CuAl catalysts and (d) to (f) used CuMg, CuMgAl-1-1 and CuAl catalysts.

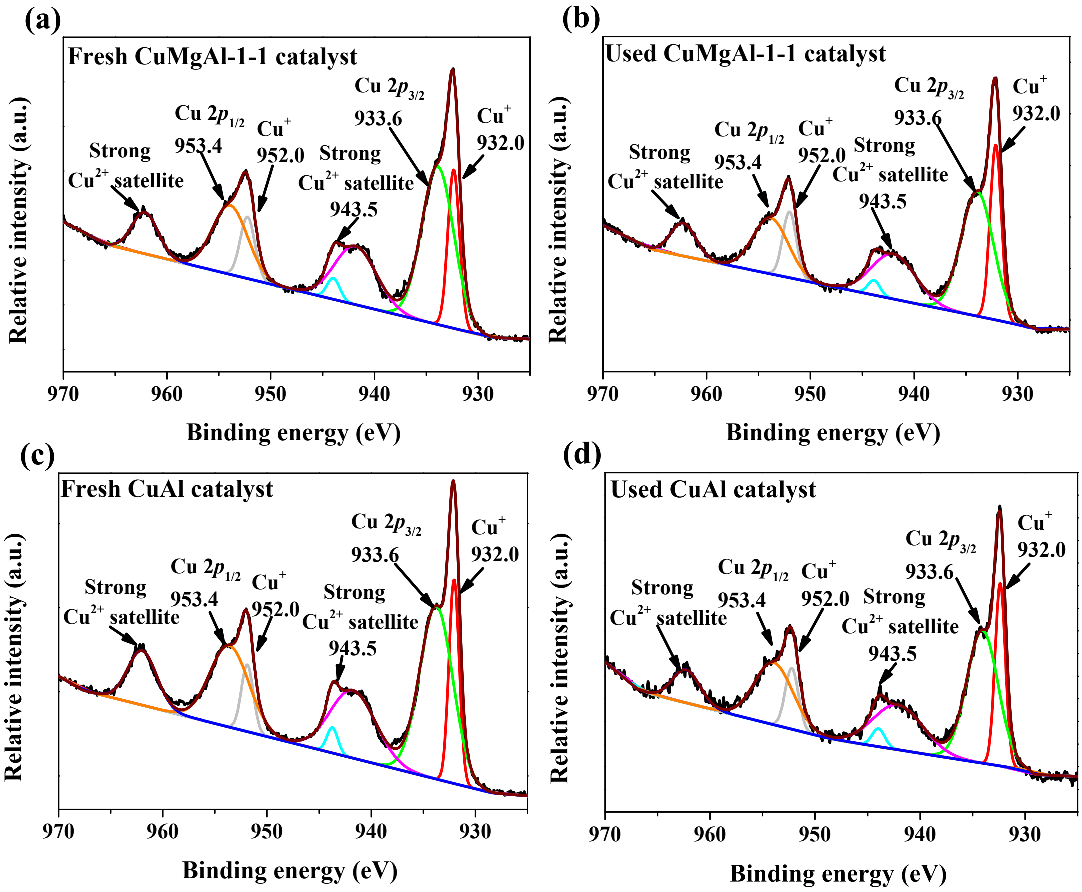


Fig. S5 The Cu 2p peaks in the high-resolution XPS spectra of CuMgAl (a) and (b) as well as CuAl catalysts (c) and (d) before and after reactions.

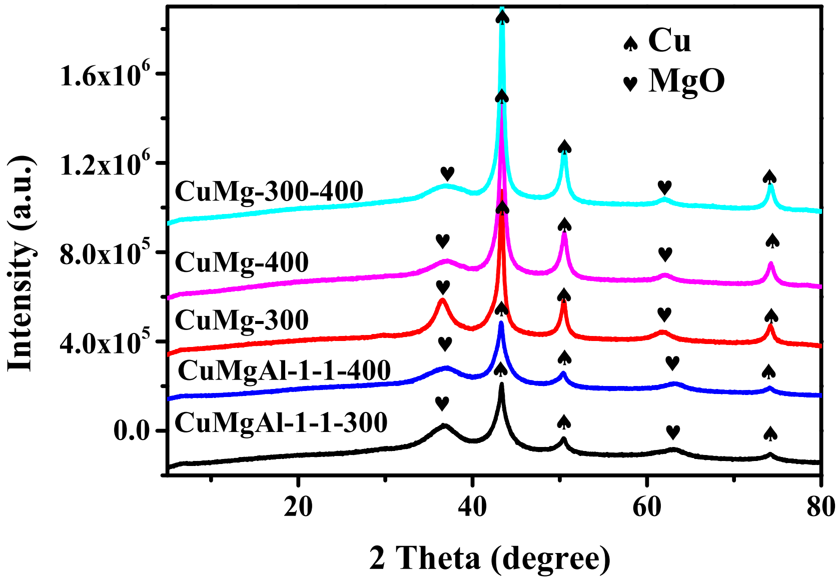


Fig. S6 XRD patterns of Cu-based catalysts reduced at different reduction temperatures. CuMgAl-1-1-300 and CuMg-300 represent that the reduced catalyst was reduced at 300°C for 2 h again. CuMgAl-1-1-400 and CuMg-400 represent that the reduced catalyst was reduced at 400°C for 2 h again. CuMg-300-400 represents that the reduced catalyst was reduced at 300°C for 2 h and then reduced at 400°C for 2 h.

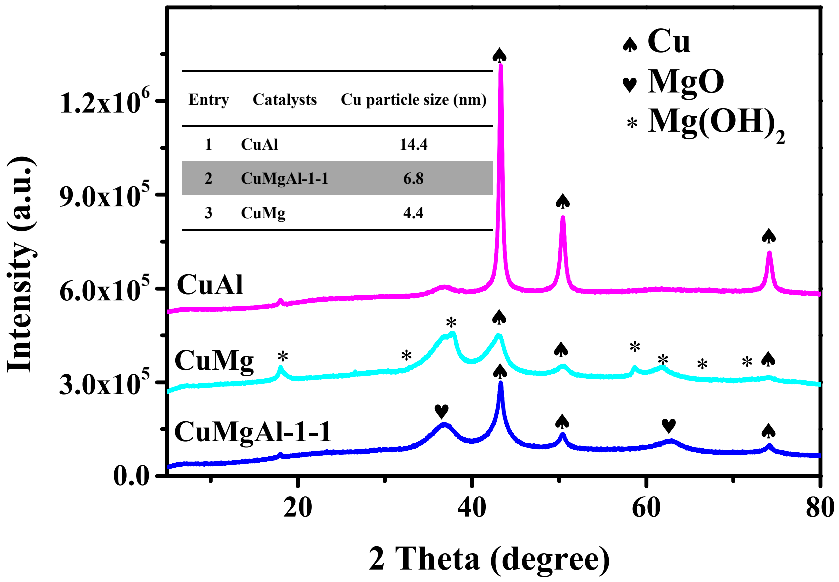


Fig. S7 XRD patterns of used Cu-based catalysts after cycle experiment at 140°C.