

Rational design of hydroxyapatite/graphite-supported bimetallic Cu-M (M = Cu, Fe, Co, Ni) catalysts for enhancing the partial hydrogenation of dimethyl oxalate to methyl glycolate

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Table S1 Physicochemical properties of the studied catalysts

Types of catalyst	SBET a (m ² g)	Dpore b (nm)	Φ_{WF}	Cu ⁺ /(Cu ⁺ +Cu ⁰) %
HAp/G/Cu 13	92	64	-	65.15
HAp/G/Cu 17	82	68	4.7 eV	56.5
HAp/G/Cu 20	74	55	-	51
HAp/G/CuFe	102	127	4.61 eV	59.15
HAp/G/CuCo	131	350	4.83 eV	50
HAp/G/CuNi	154	180	4.71 eV	16.27

Table S 2 Binding energy (eV) value of Cu element and transition metals (Co,Fe and Ni) doped HAp/G/Cu catalysts (related to Fig. 9)

Catalyst type	Cu				Co				Ni				Fe			
	2p _{3/2}		2p _{1/2}		2p _{3/2}		2p _{1/2}		2p _{3/2}		2p _{1/2}		2p _{3/2}		2p _{1/2}	
HAp/G/Cu 17	935.02	943.60	955.07	963.73												
HAp/G/CuFe	933.86	943.08	953.75	963.07									711.50	719.35	725.19	734.27
HAp/G/CuCo	934.69	943.12	954.64	963.08	781.71	785.72	797.59	803.68								
HAp/G/CuNi	935.81	943.98	955.77	963.66					857.07	862.64	874.77	880.61				

Table S3 Binding energy (eV) value of Cu element for spent catalysts (related to Fig. 13)

Types of spent catalysts	Cu			
	2p _{3/2}		2p _{1/2}	
States of elements	Cu ⁺⁰	Cu ²⁺	Cu ⁺⁰	Cu ²⁺
HAp/G/Cu 13	932.71	934.05	952.53	954.51
HAp/G/Cu 17	932.71	933.82	852.52	954.60
HAp/G/Cu 20	932.74	934.06	952.54	954.45
HAp/G/CuFe	932.82	934.43	952.63	953.68
HAp/G/CuCo	932.76	934.26	952.63	-
HAp/G/CuNi	932.71	-	952.54	-

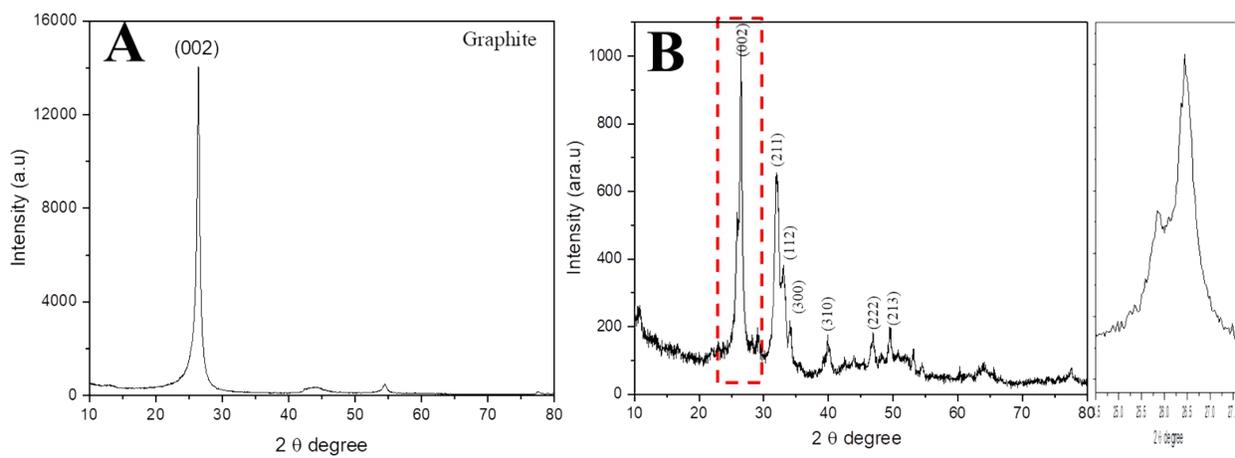


Fig. S1 XRD for (A) bare-Graphite and (B) Hydroxyapatite/Graphite composite (support material)

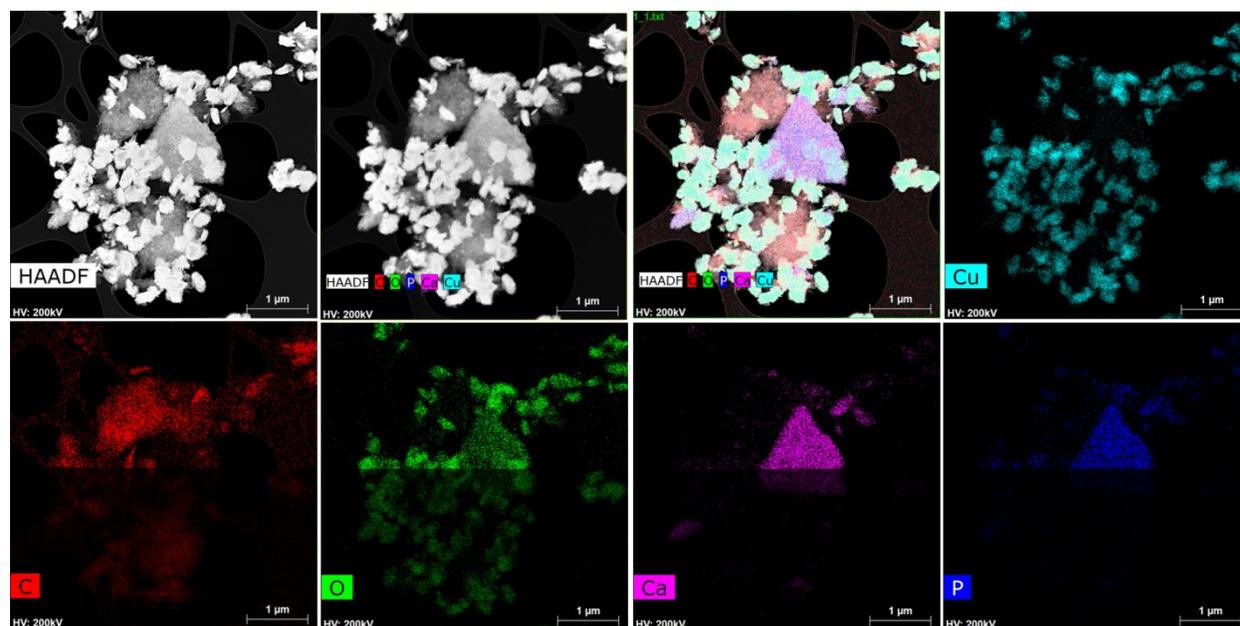


Fig. S2 (a, b) STEM/HAADF image and (c-h) EDS maps analysis of all elements of Cu/HAp/G composite catalyst.

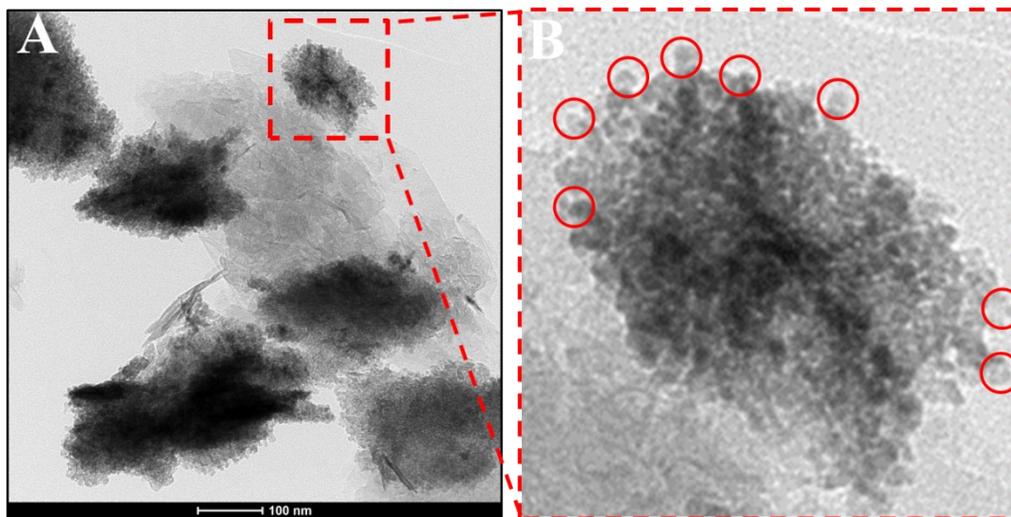


Fig. S3 (A) TEM image and (B) High magnification TEM image of HAp/G/Cu (17wt%) composite catalyst

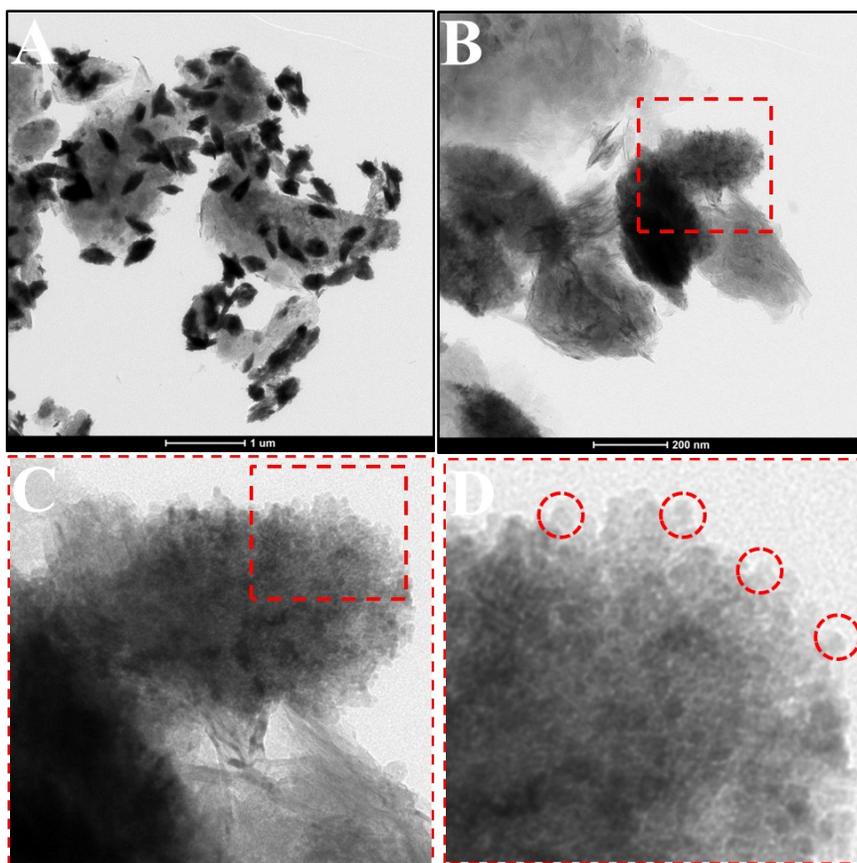


Fig. S4 (A) Low magnification TEM image and (B, C,D) High magnification TEM image of Cu/HAp/G (20 wt%) composite catalyst

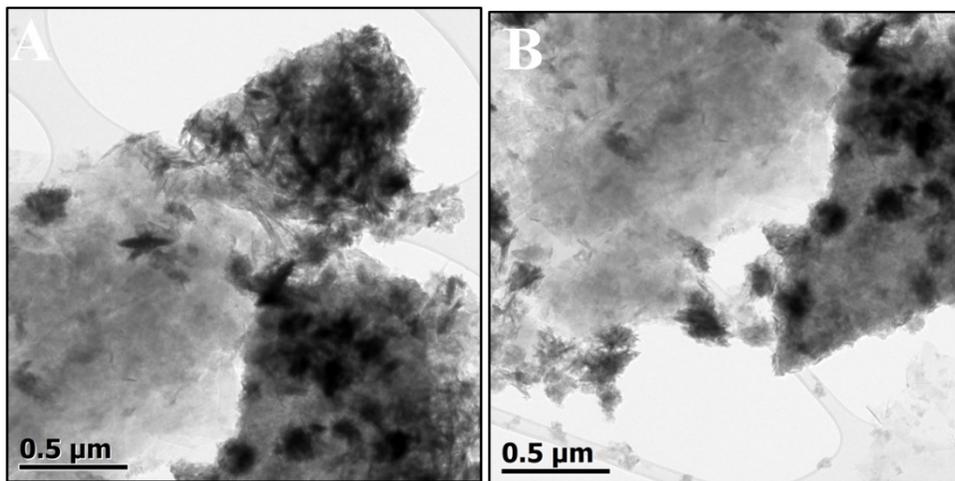


Fig. S5 (A) and (B) TEM images of HAp/G/CuCo composite catalyst

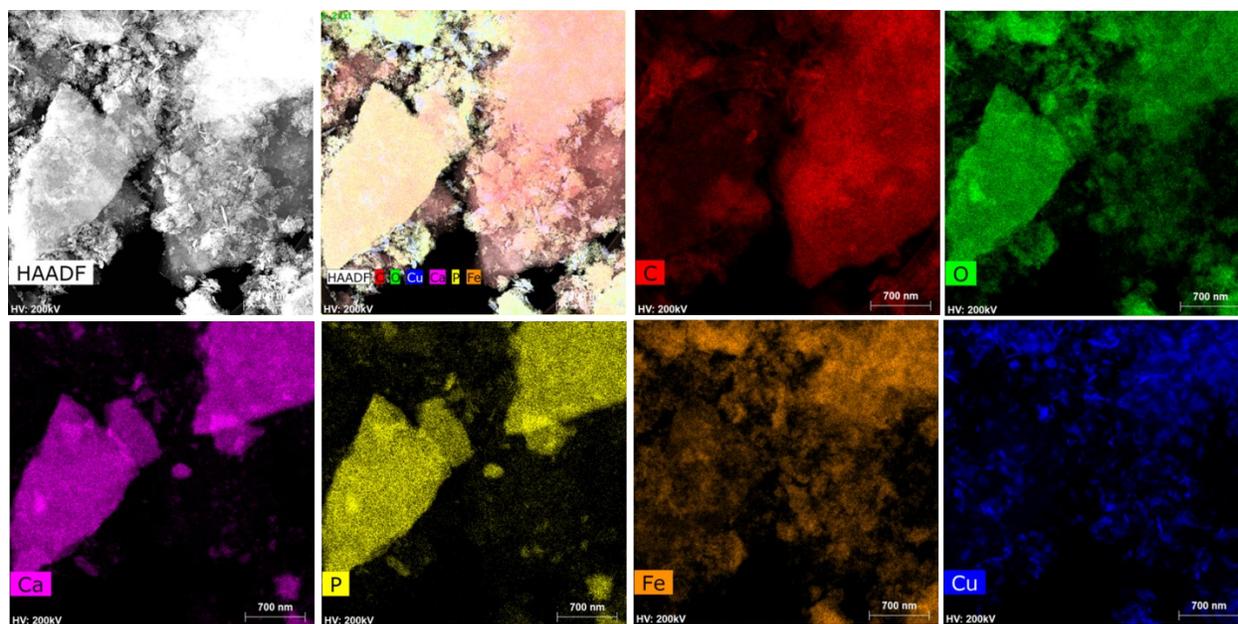


Fig. S6 (a) STEM/HAADF image and (b-h) EDS maps analysis of all elements of HAp/G/CuFe composite catalyst.

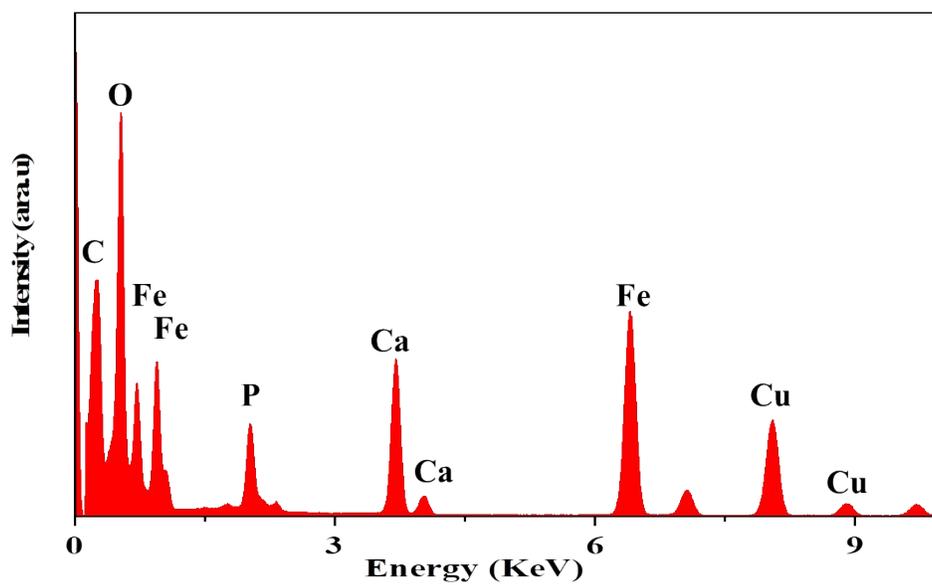


Fig. S7 EDS point analysis for HAp/G/CuFe composite catalyst

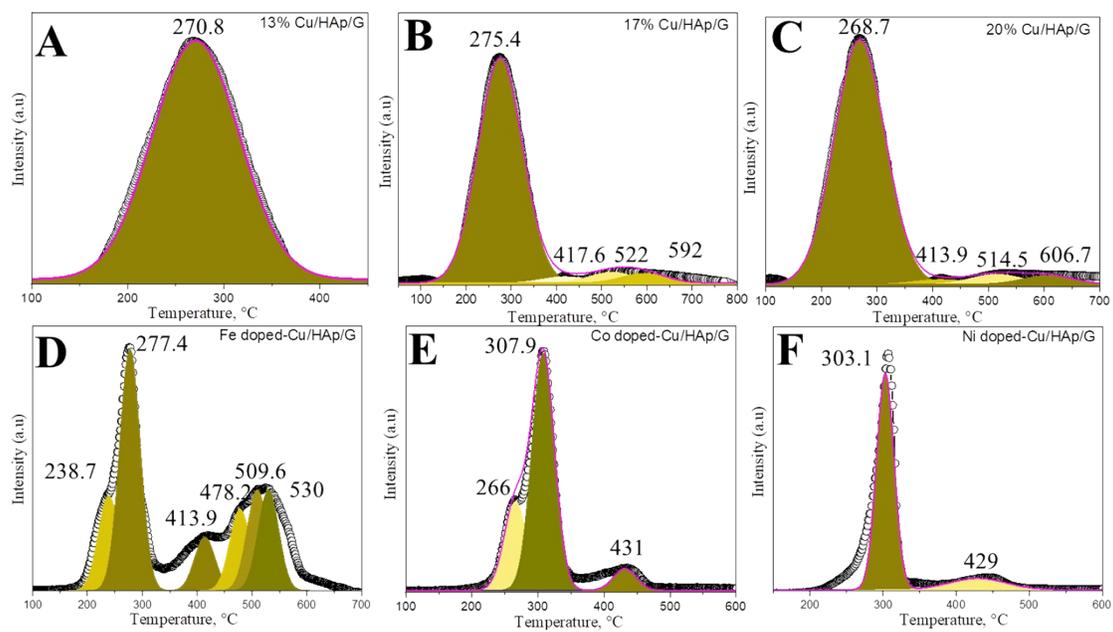


Fig. S8 H₂-TPR analysis of (A, B and C) un-doped Cu/HAp/G catalysts with different Cu loading and (D, E and F) Fe-, Co-, Ni-promoted Cu/HAp/G composite catalysts.

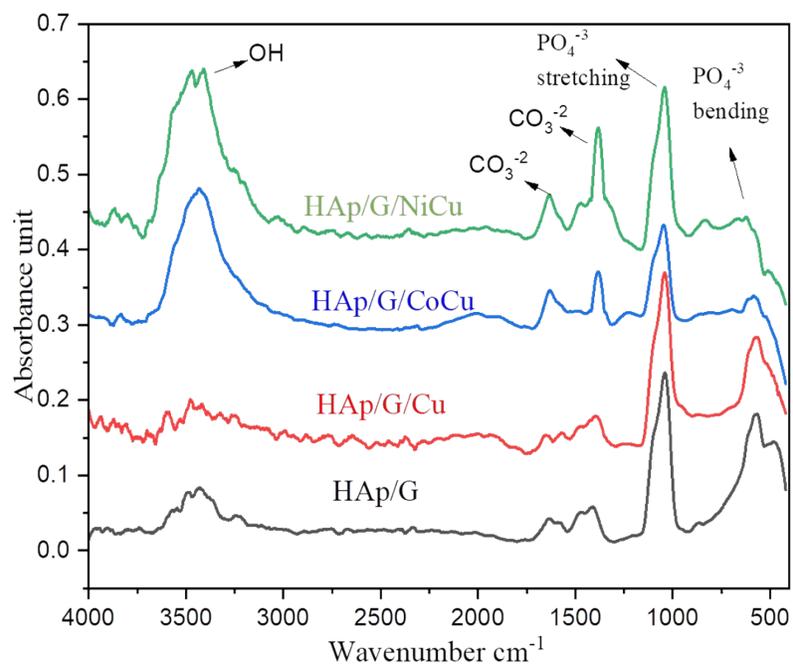


Fig. S9 FTIR of the un-promoted and Fe-, Co-, Ni-promoted HAp/G/Cu composite catalysts.

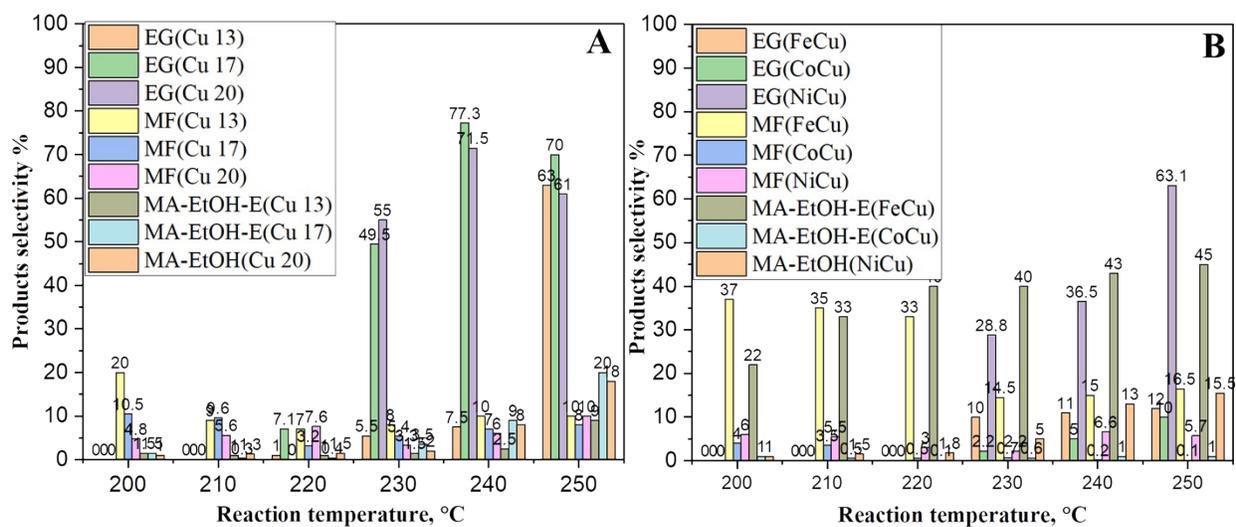


Fig. S10 Selectivity ratio of DMO hydrogenation products of (A) HAp/G/Cu catalysts with different Cu loading and (B) Fe, Co and Ni doped HAp/G/Cu catalysts. The symbols: MF: methyl formate, MA: methyl acetate, EtOH: ethyl alcohol, E: ether and EG: ethylene glycol.

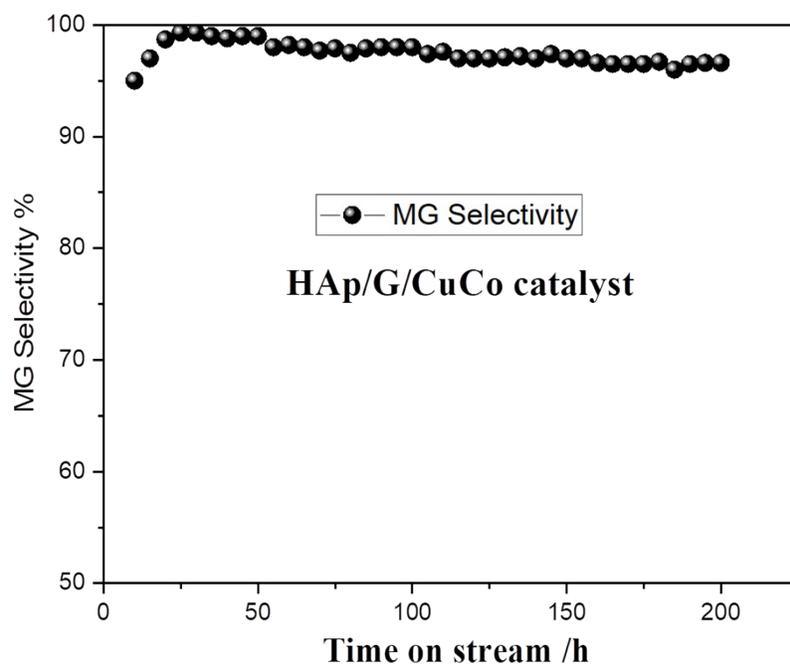


Fig. S11 Stability curve for MG selectivity of the spent HAp/G/CuCo composite catalyst after 200 h of reaction time. Reaction condition: H₂/DMO molar ratio of 200, P= 2 MPa, T=220 °C and WLHSV(DMO)=0.85 g/(g h)