Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information†

Preparation and characterization of a copper oxide nanoparticle-supported red-mud catalyst for liquid phase oxidation of ethyl benzene to acetophenone †

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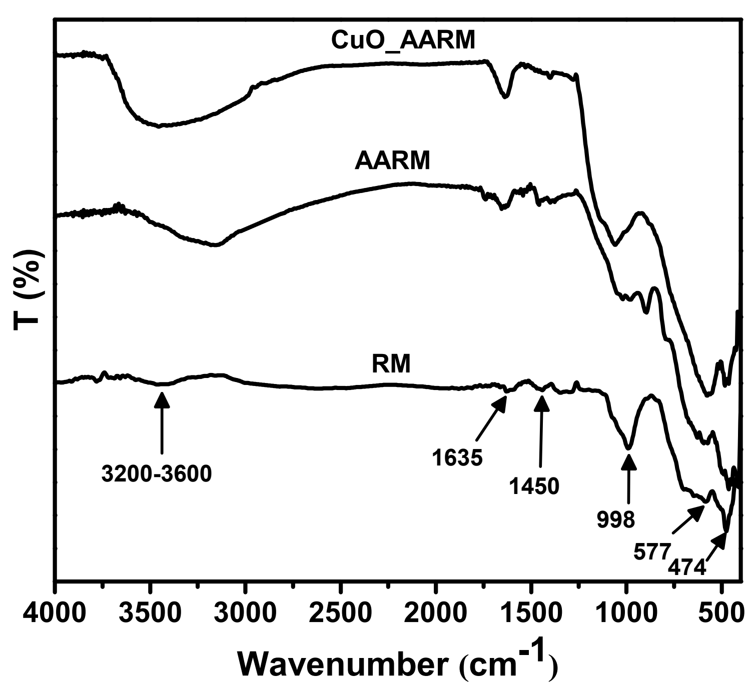
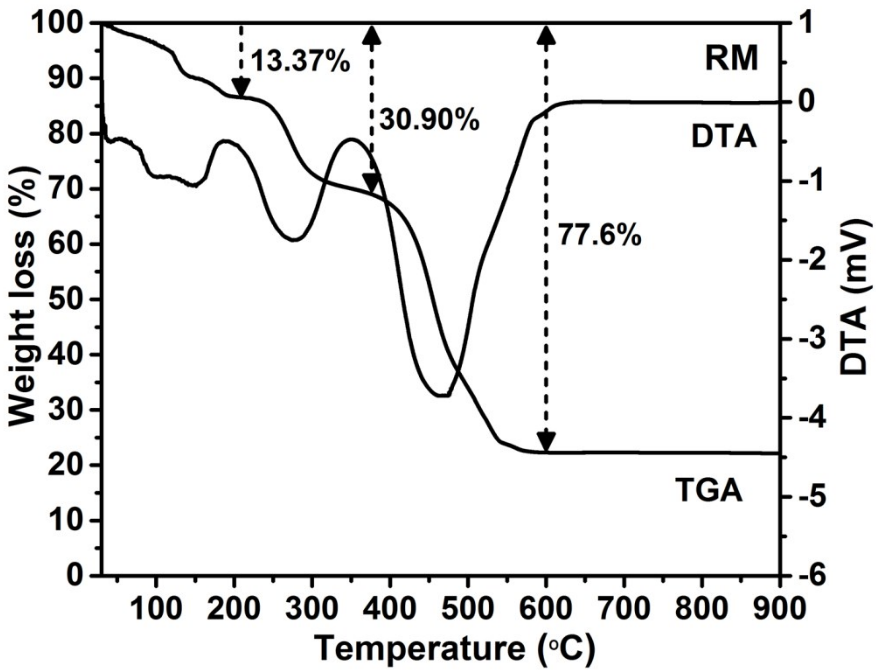


Fig. S1 FTIR spectra of RM, AARM and CuO_AARM.



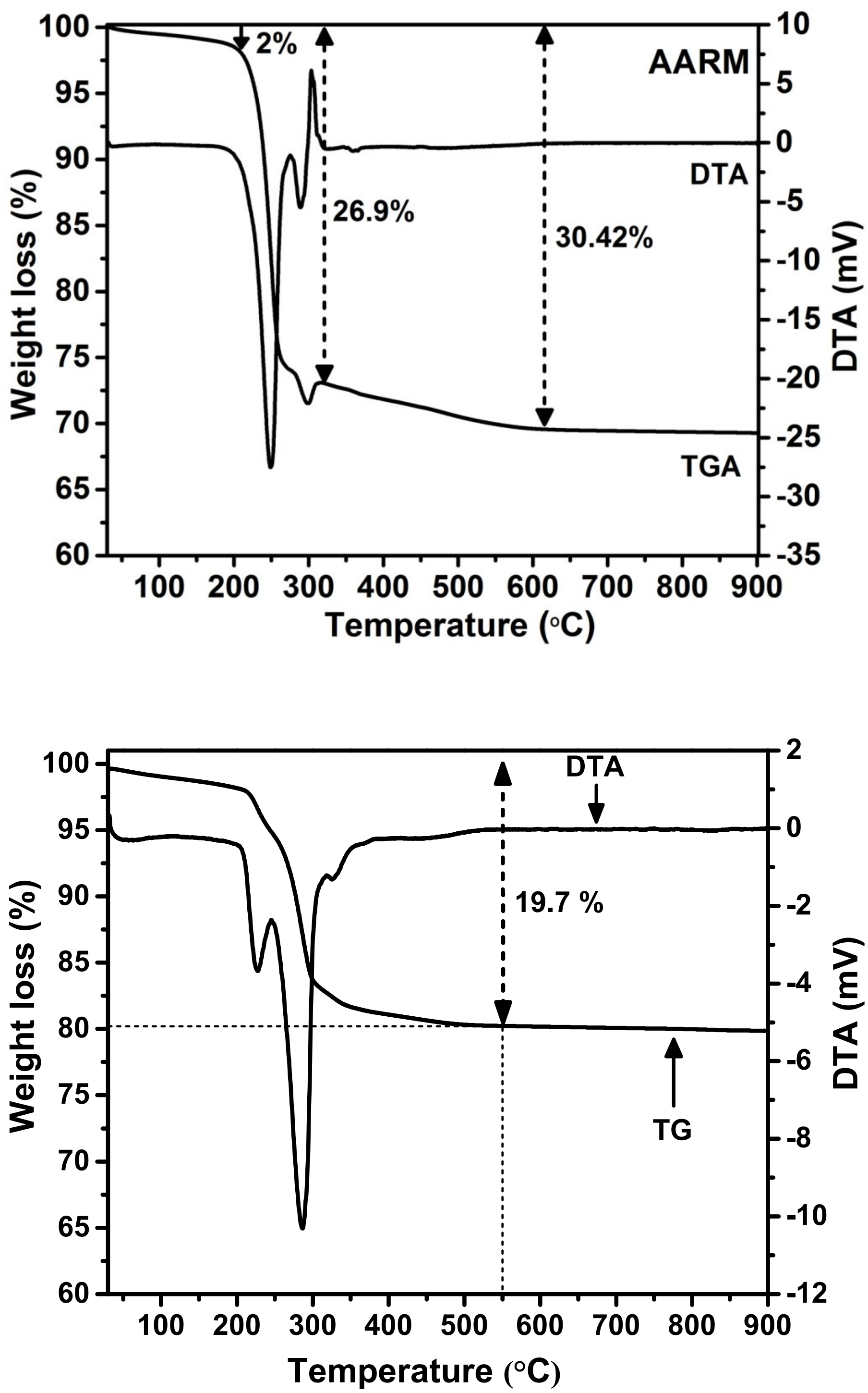


Fig. S2 DTA-TGA curve of RM and AARM and CuO_AARM (uncalcined).

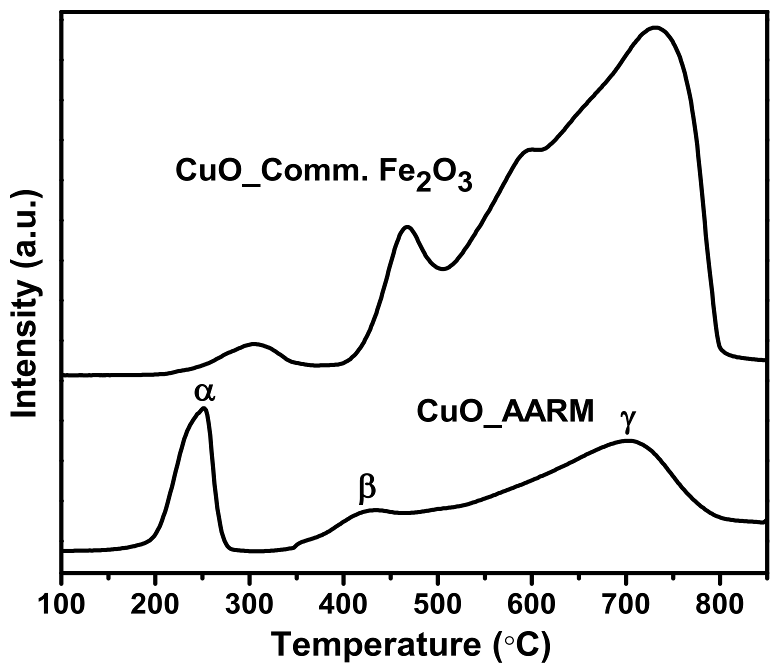


Fig. S3 H_2–TPR analysis of CuO_AARM and CuO_Comm. Fe_2O_3.

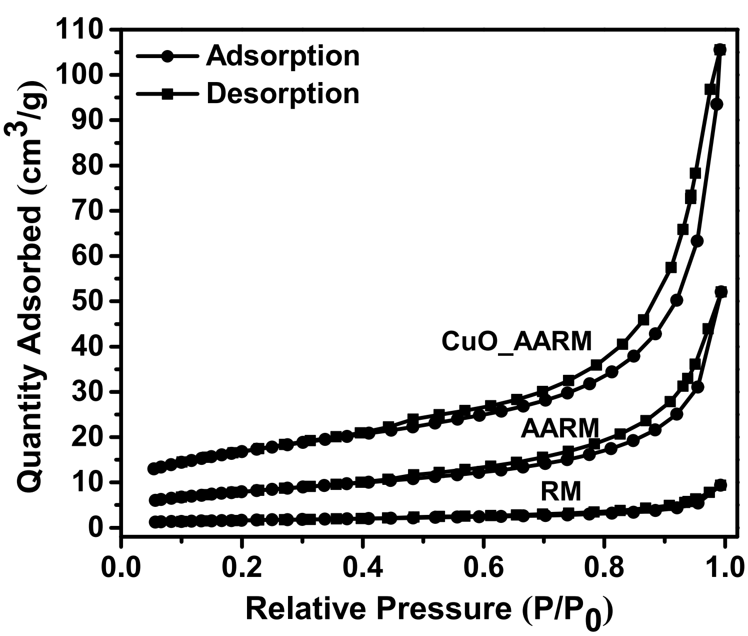


Fig. S4 N_2 adsorption/desorption isotherms for RM, AARM, CuO_AARM.

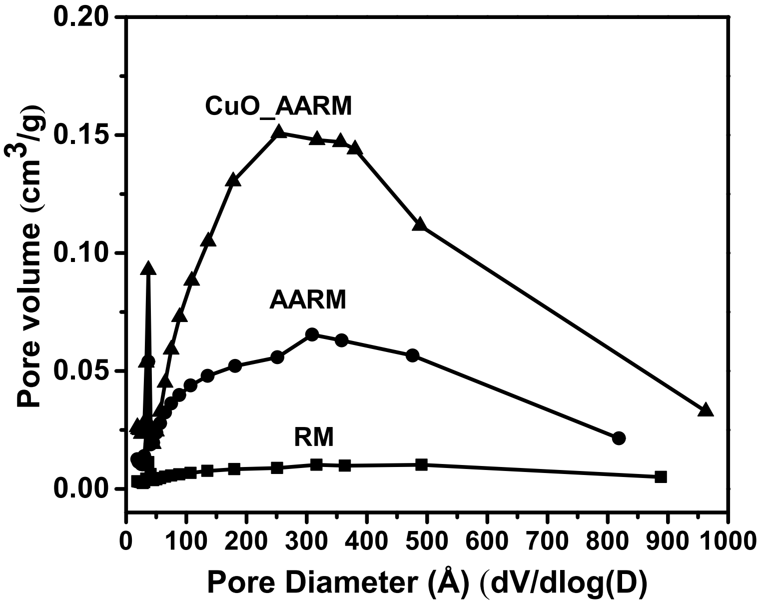


Fig. S5 Distribution of pore diameters in RM, AARM and CuO_AARM.

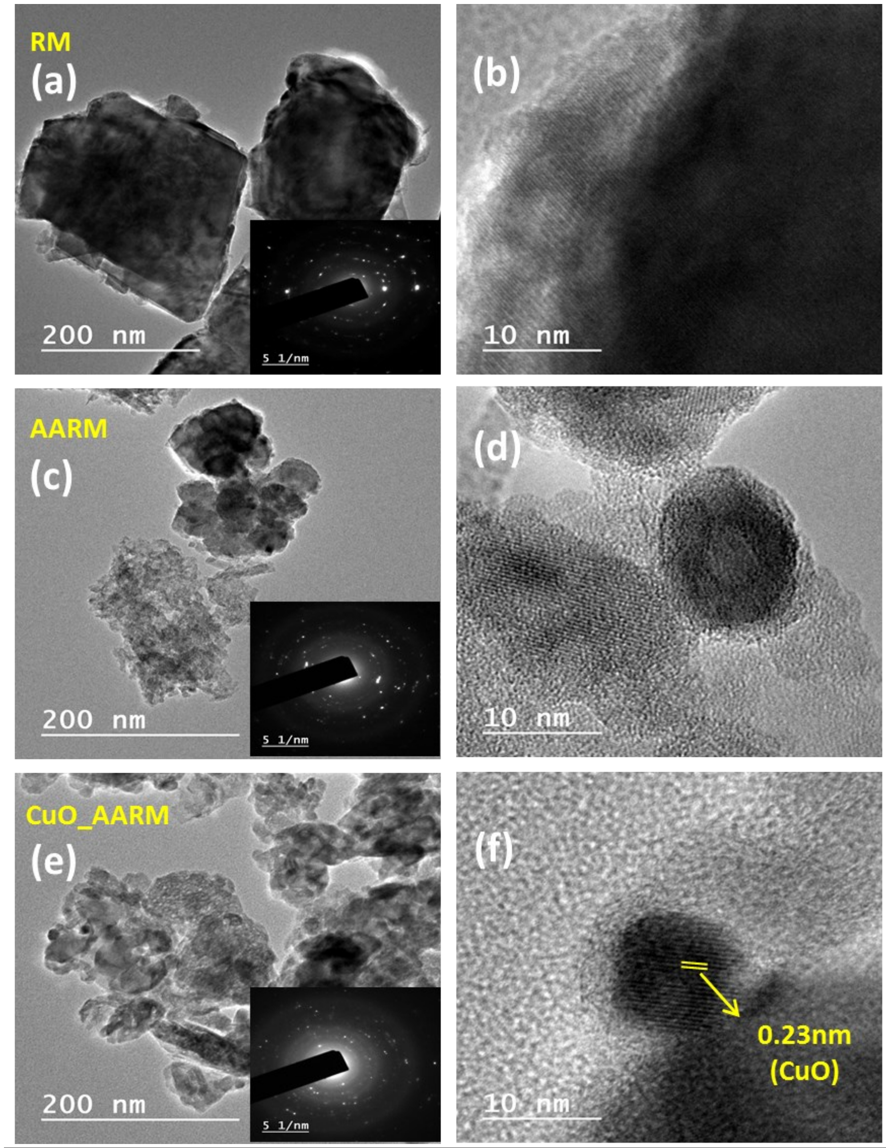


Fig. S6 TEM images (a, c, & e) and HR-TEM (b, d, & f) of RM, AARM and CuO_AARM respectively; the inset images of (a), (c), and (e) show the SAED pattern of the corresponding samples

EDAX analysis and mapping of RM, AARM and CuO_AARM (catalyst) materials

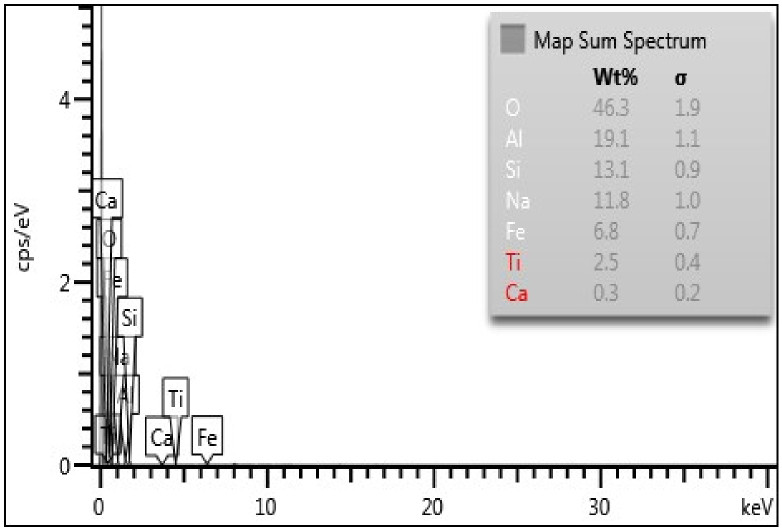


Fig. S7(a) Elemental analysis of Red Mud (RM)

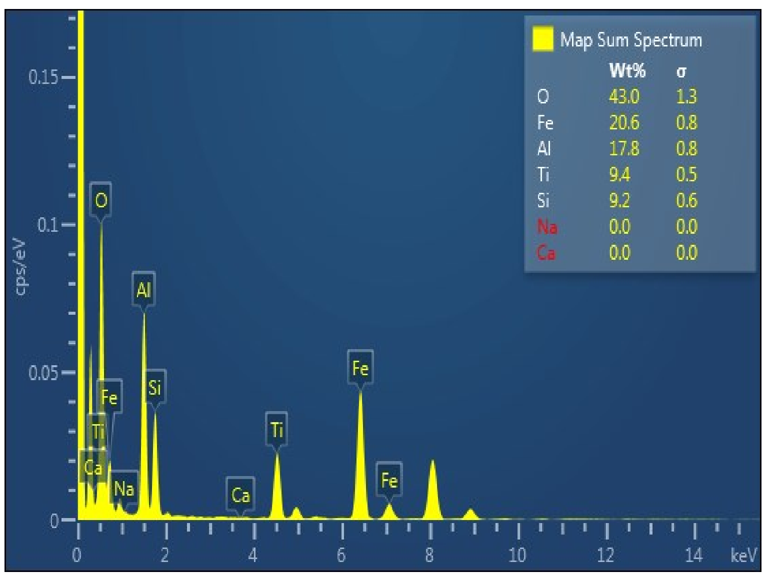


Fig. S7(b) Elemental analysis of AARM

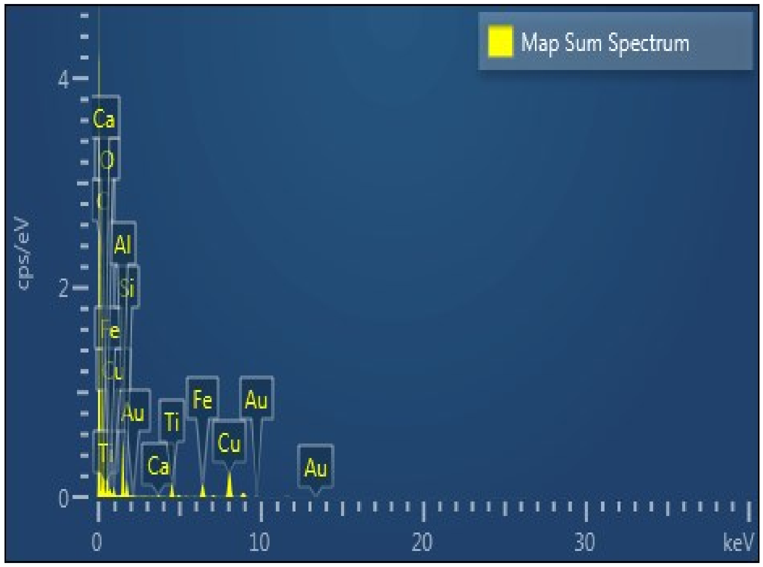


Fig. S7(c) Elemental analysis of CuO_AARM

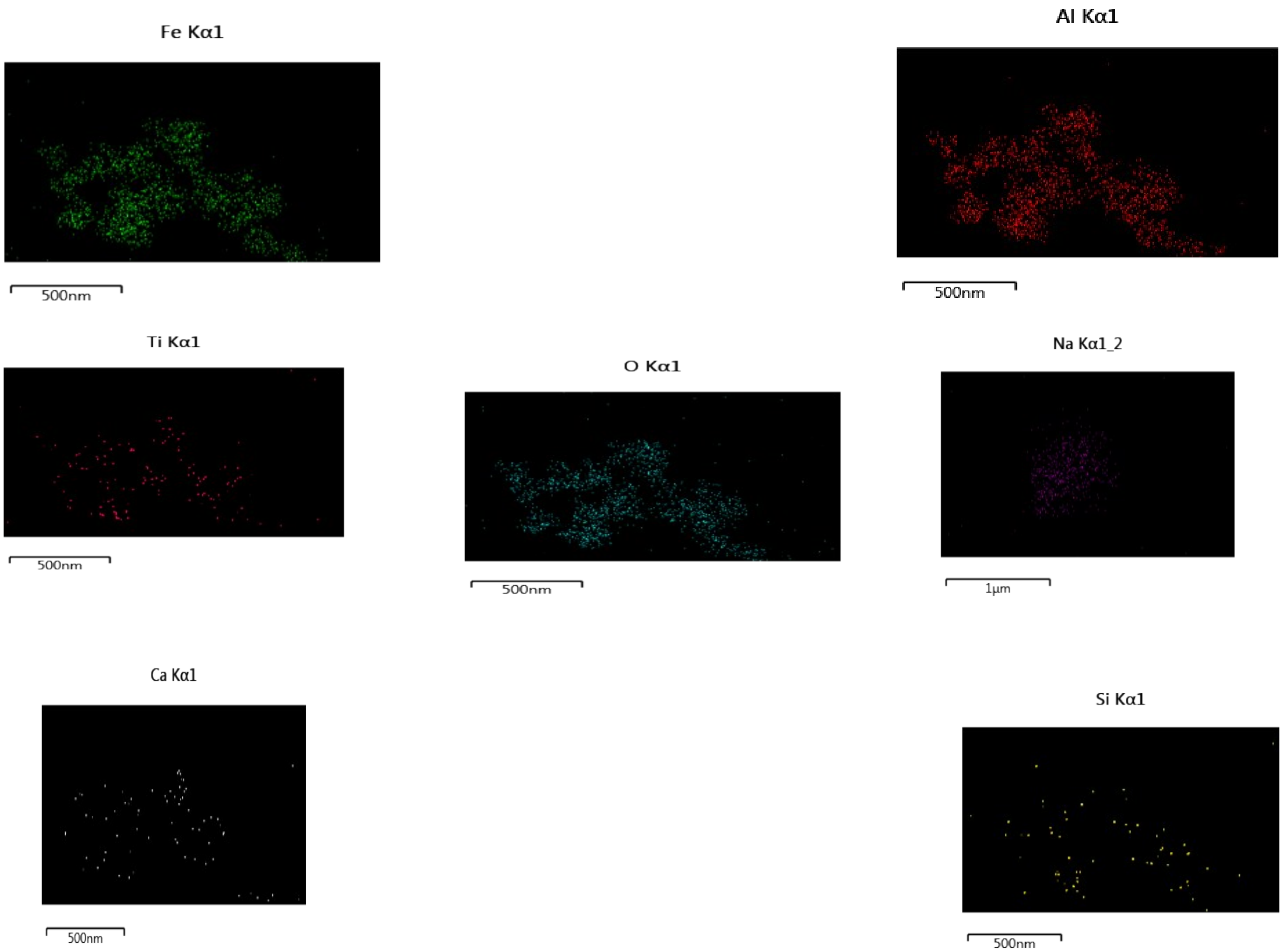


Fig. S7(d) Elemental mapping of RM

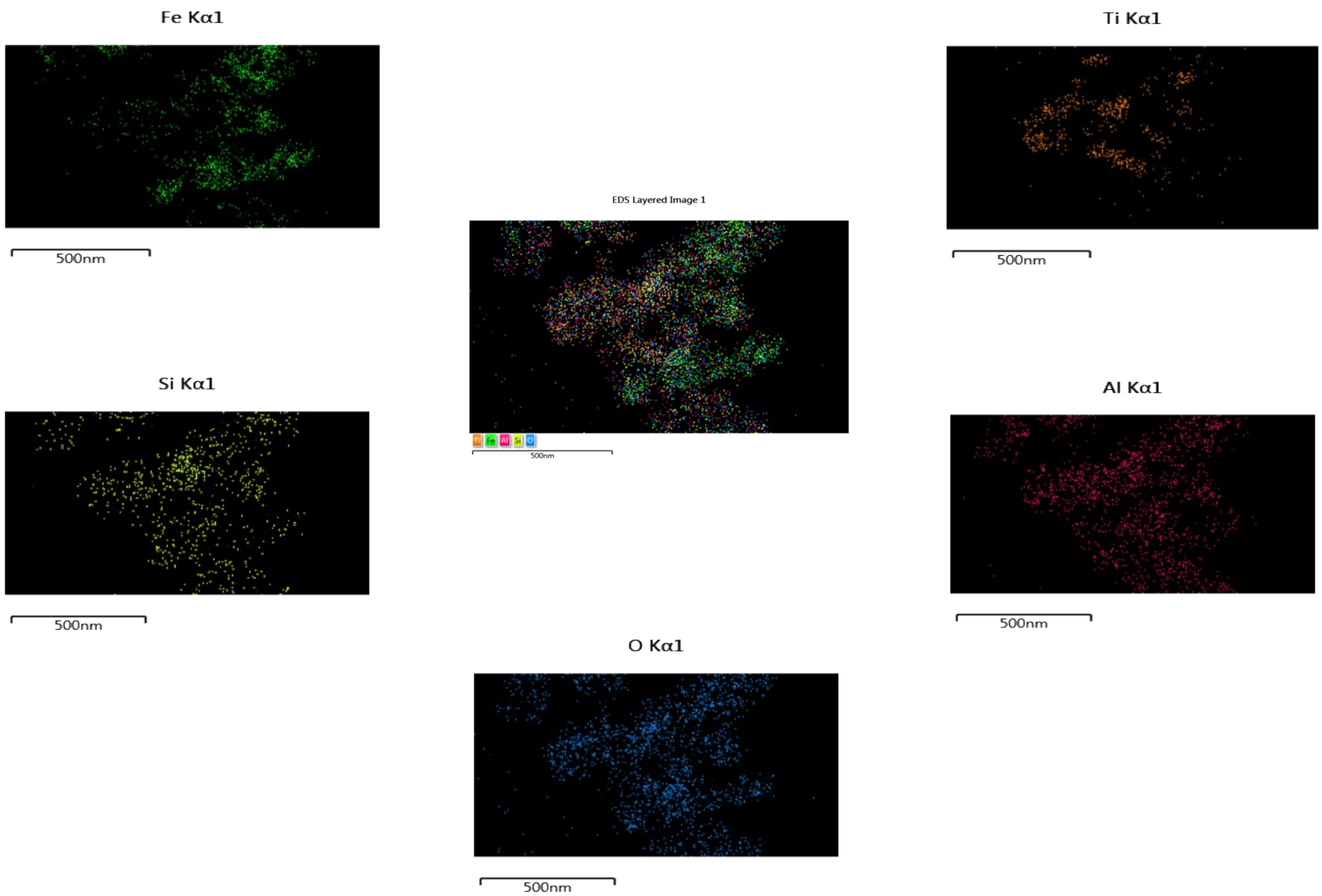


Fig. S7(e) Elemental mapping of AARM

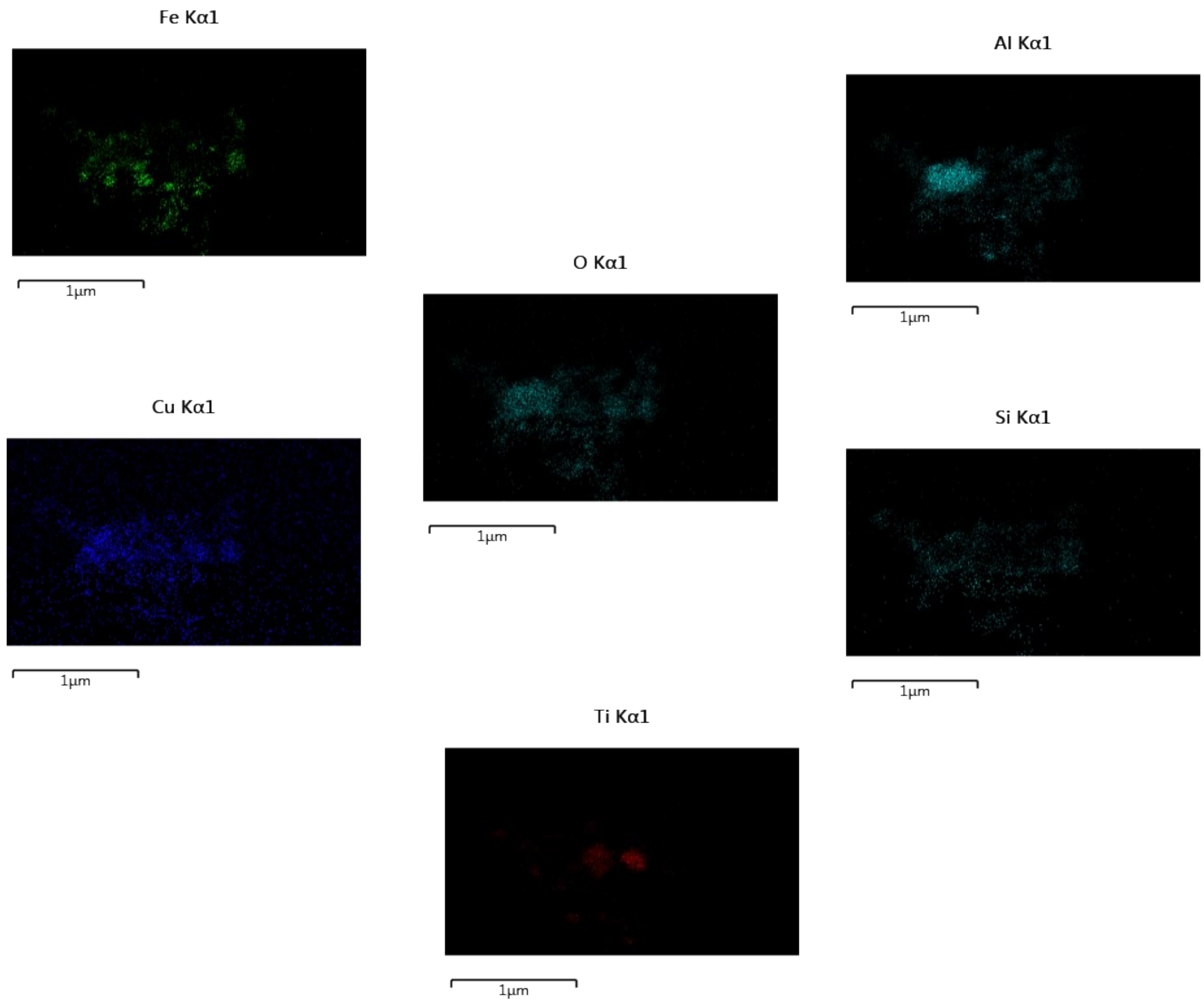


Fig. S7(f) Elemental mapping of CuO-AARM

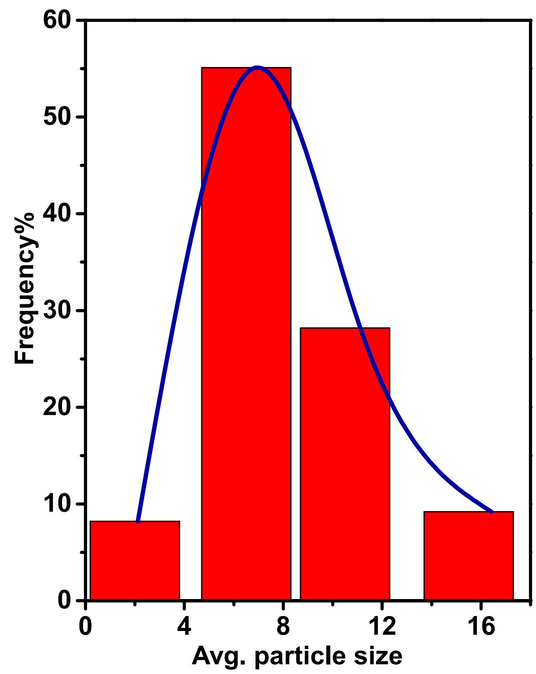


Fig. S8 Average particle size of CuO_AARM

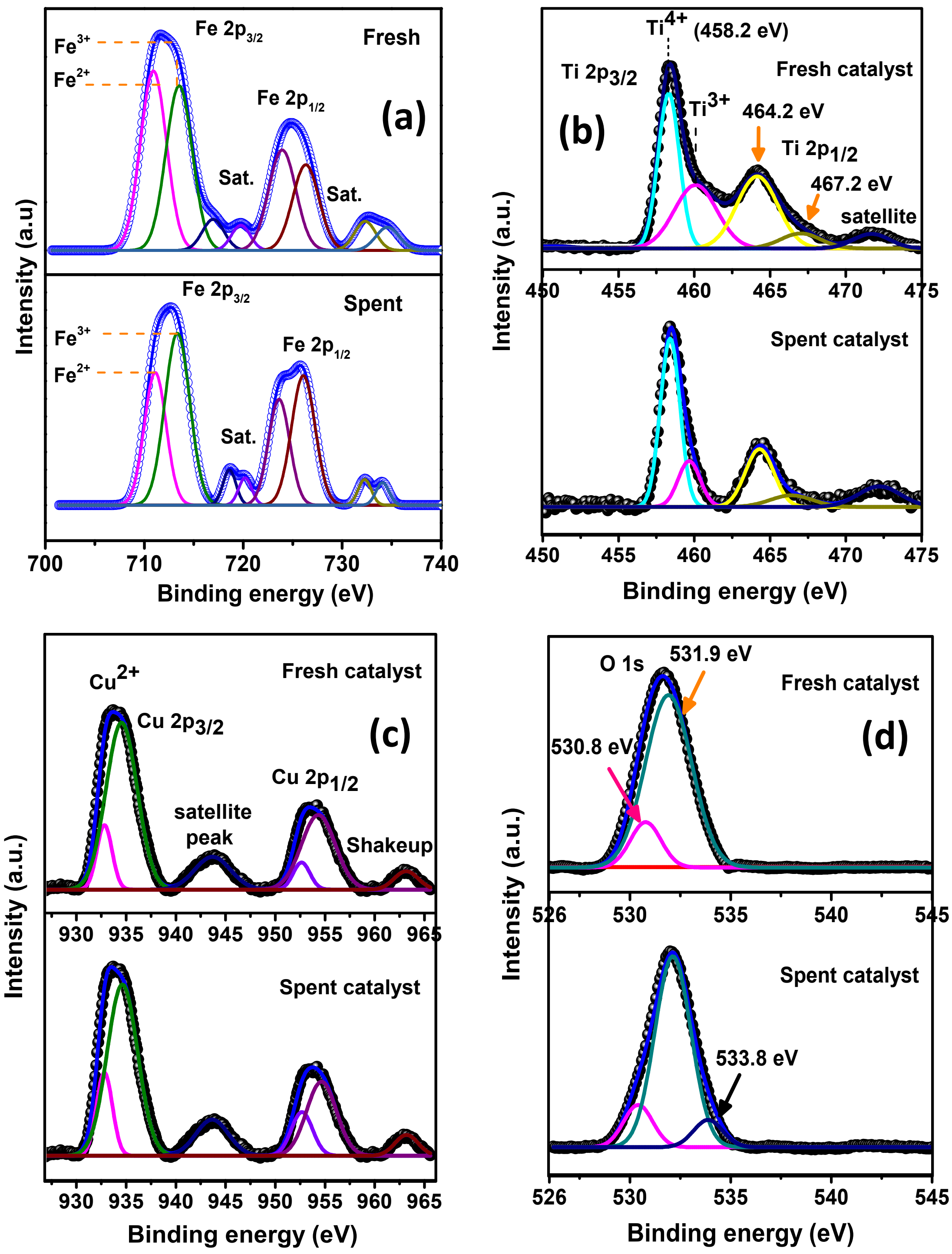


Fig. S9 XPS spectra: deconvolution of (a) Fe 2p fresh and spent catalyst, (b) Ti 2p fresh and spent catalyst, (c) Fresh and spent catalyst of Cu 2p, and (d) fresh and spent spectra of O1s.

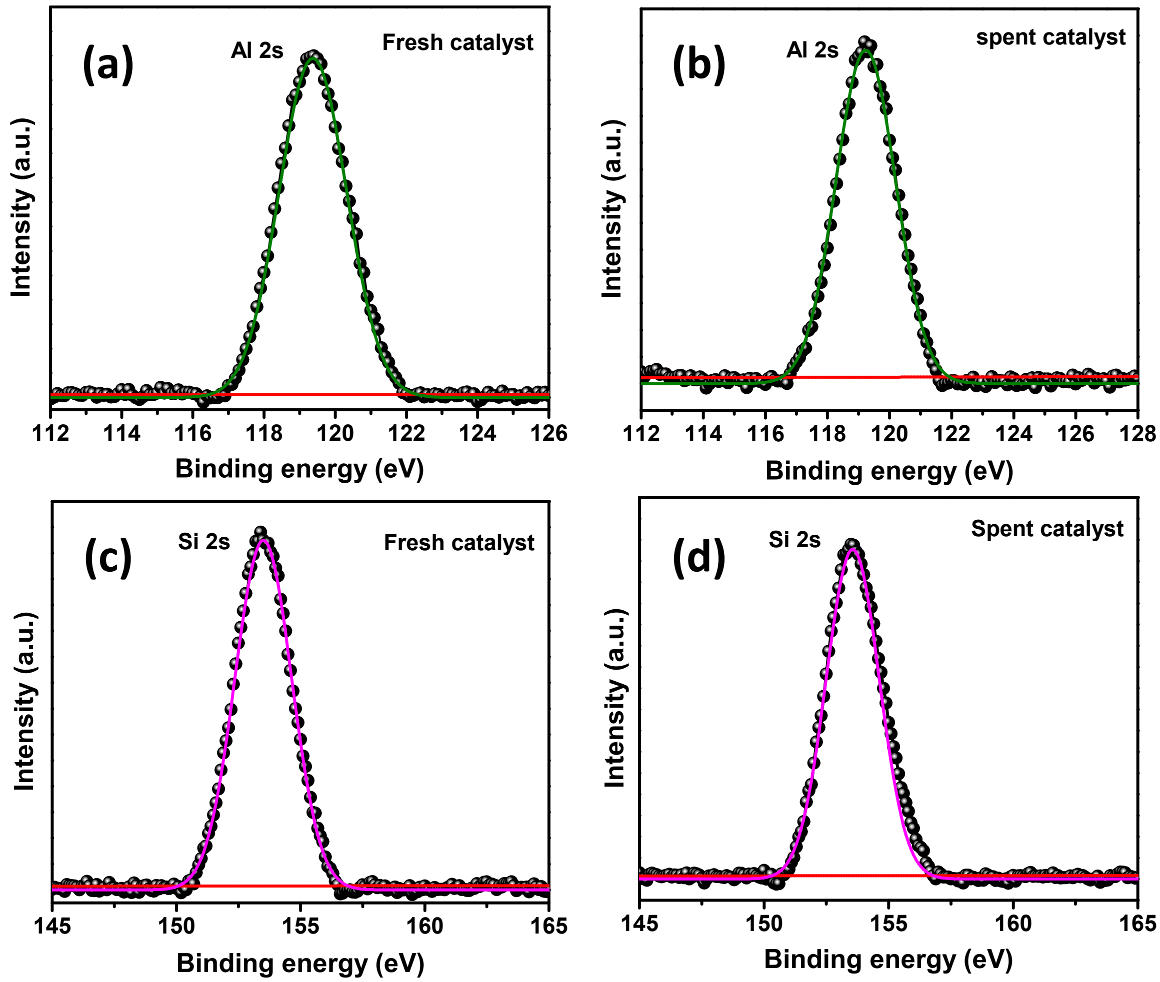


Fig. S10 XPS spectra of: Al 2s (a) fresh (b) spent catalyst; Si 2s (a) fresh (b) spent catalyst

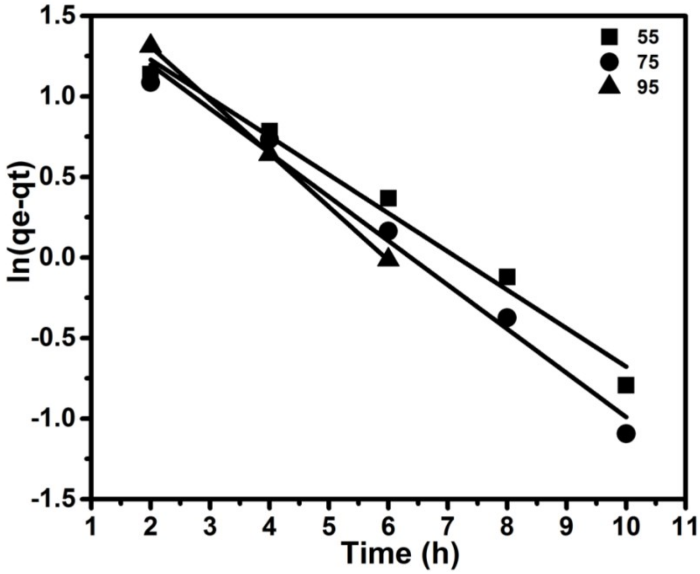


Fig. S11(a) Kinetic plot of $\ln(q_e\text{-}q_t)$ *vs.* t (pseudo 1^{st} order) at different temperatures

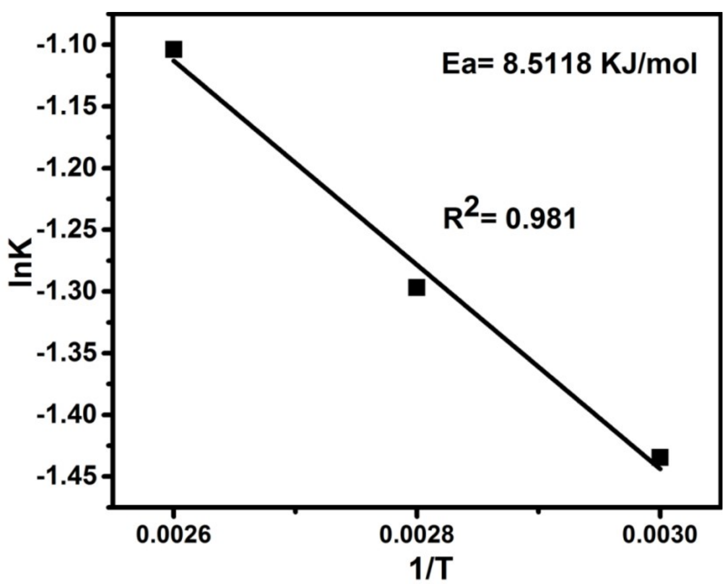


Fig. S11(b) Arrhenius plot (plot of $\ln k_1$ *vs*. T^{-1})

Table S1. Activities of catalyst with variation of solvents

Catalyst	Solvent	Reaction condition	Conversion	Selectivity of acetophenone	Selectivity of benzaldehyde
CuO_AARM	Acetone	45 °C, 2mol, 50wt% H_2O_2, 12h	22%	45%	7%
	H_2O	75 °C, 2mol, 50 wt% H_2O_2, 12h	47%	55%	10%
	Acetonitrile	75 °C, 2mol, 50 wt% H_2O_2, 12h	86%	74%	8.33%
	H_2O and Acetonitrile (1:1)	75 °C, 2 mol, 50 wt% H_2O_2, 12h	69%	68%	10%

Table S2. Comparative aspects with commercial materials (literature reported)

Sl No.	Catalyst(s)	Solvent	Reaction Condition(s)	Conversion/Selectivity/ Yield (%)	Ref.
1	Ag/ZnO	Solvent-free	80 °C, 1-mol H_2O_2, 7 h	90/-/90	13
2	Pd/g-C_3N_4-rGO	Acetonitrile	80 °C, 4-mol TBHP, 24 h	67/97/-	6
3	MnFeSi Composite	Acetone	50 °C, 1mol H_2O_2,6 h	5.5/> 90/-	9
4	Co-Cu Mixed metal oxide	Solvent-free	120 °C, 3-mol TBHP,12 h Nitrogen atmosphere	92.8/89.4/-	16
5	Phenyl group incorporated supported Co_3O_4 oxide	Solvent-free	120 °C, 10 bar, 6 h	55.1/86.1/-	43
6	CuO_AARM	Acetonitrile	75°C, 2-mol H_2O_2 12 h.	86/74/-	Present work

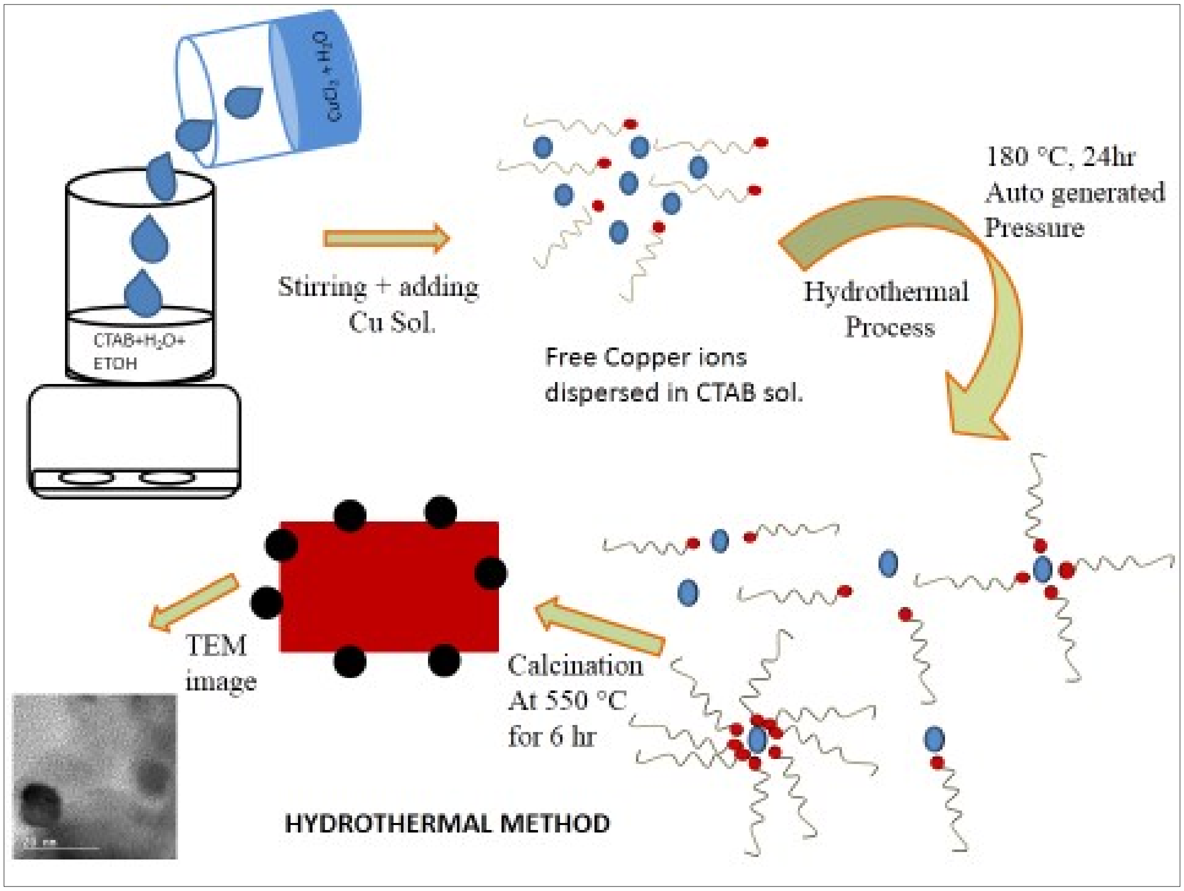
Table S3. The Thermodynamics table

Sl. No.	Temperature (°C)	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1} K^{-1})
1.	55	-10217.3	21430.0	96.7
2.	75	-12393.7		
3.	95	-14066.7		

Table S4. DFT calculation table

	Vacuum (E_h)	Acetonitrile (E_h)	Solvation Energy (E_h)
1	-310.658068	-310.6631656	-0.00509755
2	-385.8751983	-385.885636	-0.01043773
2'	-310.0303283	-310.0349634	-0.00463509
3	-385.8703337	-385.8819787	-0.01164493
3'	-310.0060882	-310.010919	-0.00483071
4	-385.2179098	-385.228023	-0.01011317
5	-345.4223515	-345.4320303	-0.00967878
6	-115.6812063	-115.6896159	-0.00840953
7	-461.0016336	-461.0156316	-0.013998
8	-384.7034132	-384.7139126	-0.0104994
H_2O_2	-151.5466169	-151.5593912	-0.01277425
$OH^{\bullet}$	-75.74340475	-75.75107048	-0.00766573
H_2O	-76.42241691	-76.43491747	-0.01250056
H_2	-1.17431929	-1.17468111	-0.00036182
$H^{\bullet}$	-0.498762812	-0.498919271	-0.000156459

1 → 2'	81.12539416	kcal/mol
1 → 3'	96.21337121	kcal/mol
S_1	367.6228145	kcal/mol
S_2	-16.46189488	kcal/mol
S_3	-89.45225946	kcal/mol
S_4	20.23323811	kcal/mol
S_5	-66.52446072	kcal/mol
S_6	-161.5161849	kcal/mol



Scheme S1. Pictorial representation of synthesis procedure (hydrothermal technique)

Scheme S2. Decomposition of H_2O_2 in presence of Fe

$$Fe^{2+} + H_2O_2 \rightarrow OOH^{\cdot} + H^{\cdot} \qquad i)$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\cdot} + OH^{\cdot} \qquad ii)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O + O^{\cdot} \qquad iii)$$

$$OOH^{\cdot} + H^{\cdot} \rightarrow H^{\cdot} + O_2^{\cdot} + H^{\cdot} \qquad \text{iv)}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H^{\cdot} + OH^{\cdot} + O^{\cdot} \qquad v)$$

$$H^{\cdot} + OH^{\cdot} + O^{\cdot} \rightarrow H^{\cdot} + O^{\cdot} + O^{\cdot} + H^{\cdot} \qquad vi)$$

$$OOH^{\cdot} + H^{\cdot} \rightarrow H^{\cdot} + OH^{\cdot} + O^{\cdot} \qquad \text{vii)}$$

$$OOH^{\cdot} + H^{\cdot} \rightarrow H^{\cdot} + OH^{\cdot} + O. \qquad viii)$$

$$H^{\cdot} + O_2^{\cdot} + H^{\cdot} \rightarrow H^{\cdot} + O^{\cdot} + O^{\cdot} + H^{\cdot} \qquad \text{ix)}$$

Scheme S3. Pictorial (videography) presentation of formation of acetophenone using DFT calculation.