CoCuAl layered double hydroxides – Efficient solid catalysts for the preparation of industrially important fatty epoxides

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Electronic Supplementary Information

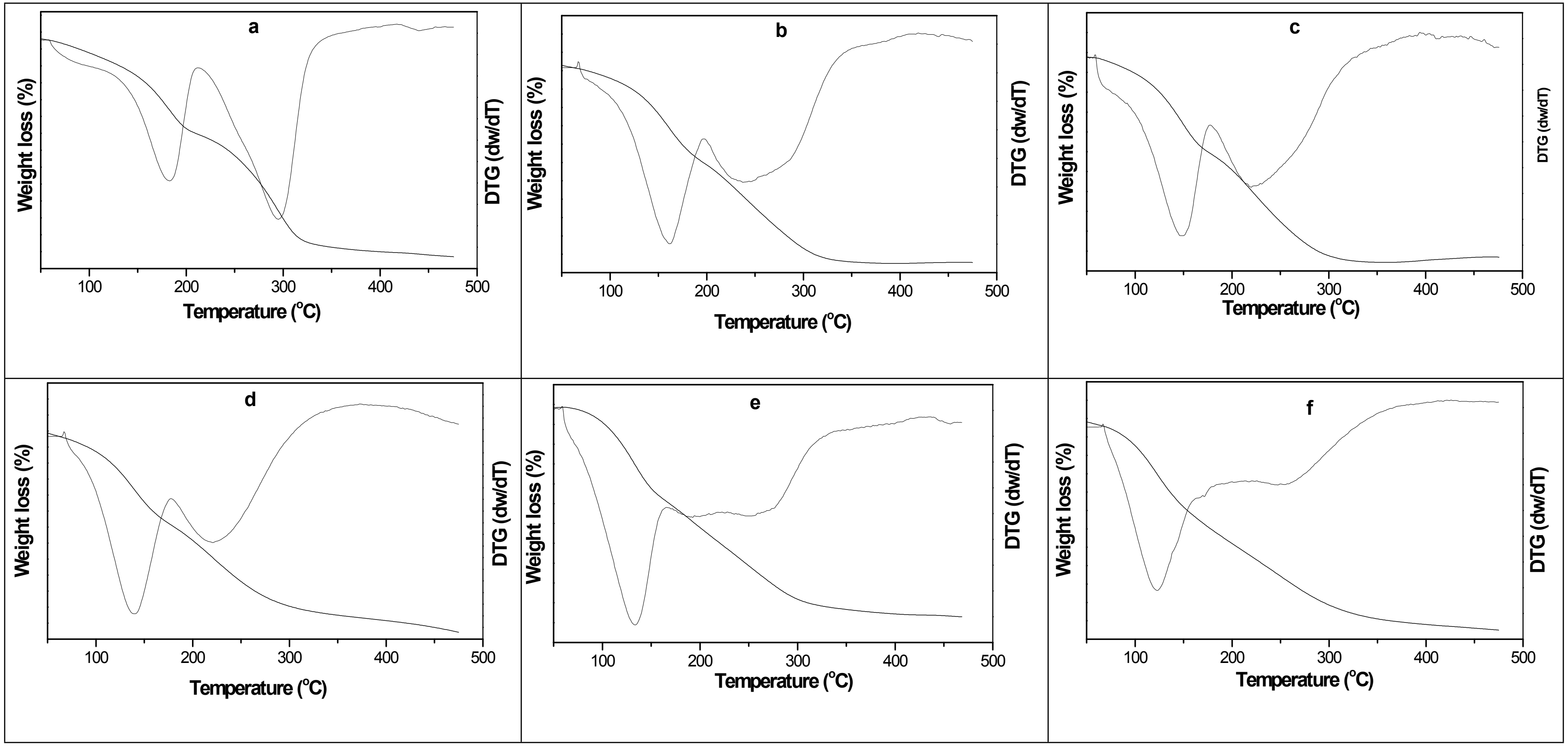


Fig. S1. TGA-DTGA profile of (a) $Co_{100}Cu_0Al$-LDH, (b) $Co_{90}Cu_{10}Al$-LDH, (c) $Co_{70}Cu_{30}Al$-LDH, (d) $Co_{50}Cu_{50}Al$-LDH, (e) $Co_{30}Cu_{70}Al$-LDH, (f) $Co_{10}Cu_{90}Al$-LDH

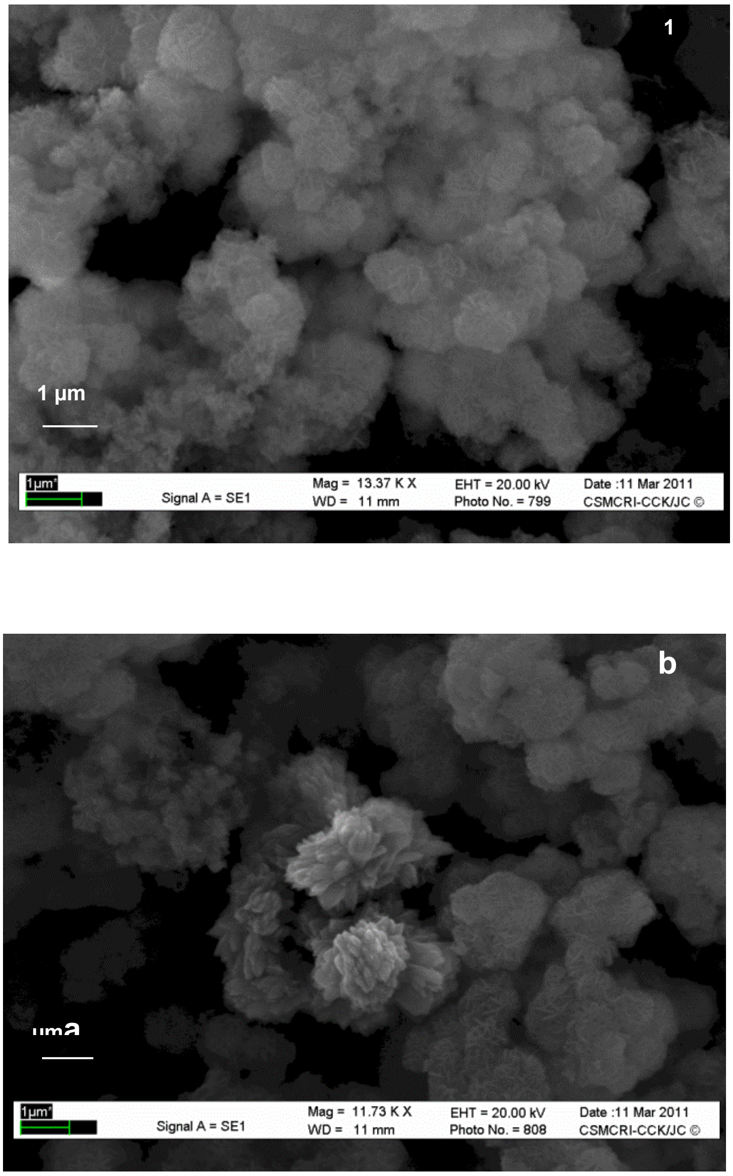


Fig. S2. SEM analysis of (a) $Co_{30}Cu_{70}Al$-LDH, (b) $Co_{10}Cu_{90}Al$-LDH

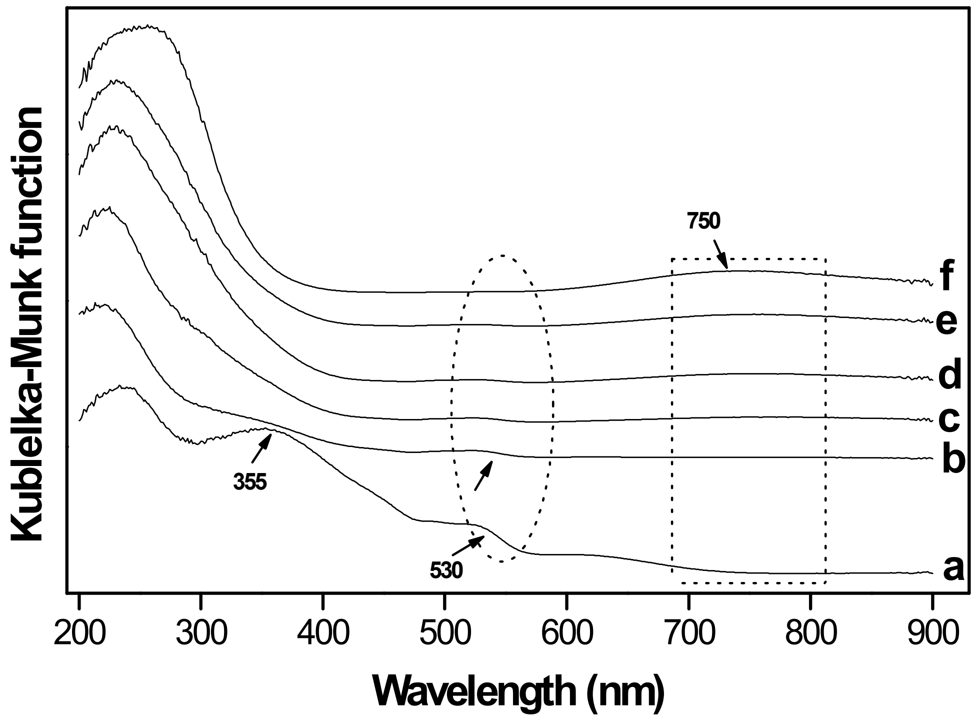


Fig. S3. UV-vis DRS analysis of (a) $Co_{100}Cu_0$Al-LDH, (b) $Co_{90}Cu_{10}$Al-LDH, (c) $Co_{70}Cu_{30}$Al-LDH, (d) $Co_{50}Cu_{50}$Al-LDH, (e) $Co_{30}Cu_{70}$Al-LDH, (f) $Co_{10}Cu_{90}$Al-LDH

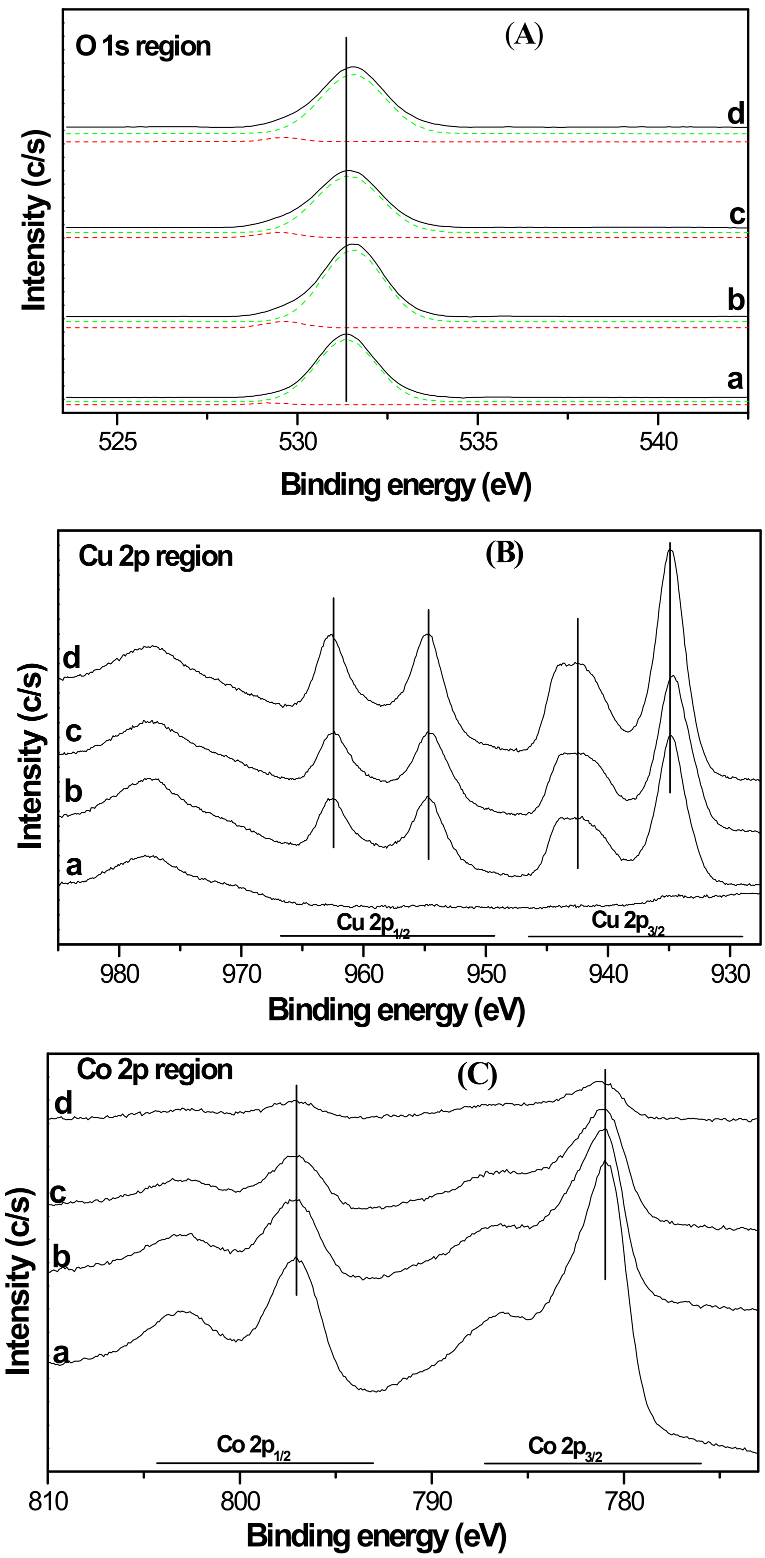


Fig. S4. (A) O 1s XP spectra, (B) Cu 2p XP spectra and (C) Co 2p XP spectra for (a) $Co_{100}Cu_{0}$Al-LDH, (b) $Co_{50}Cu_{50}$Al-LDH, (c) $Co_{30}Cu_{70}$Al-LDH, (d) $Co_{10}Cu_{90}$Al-LDH

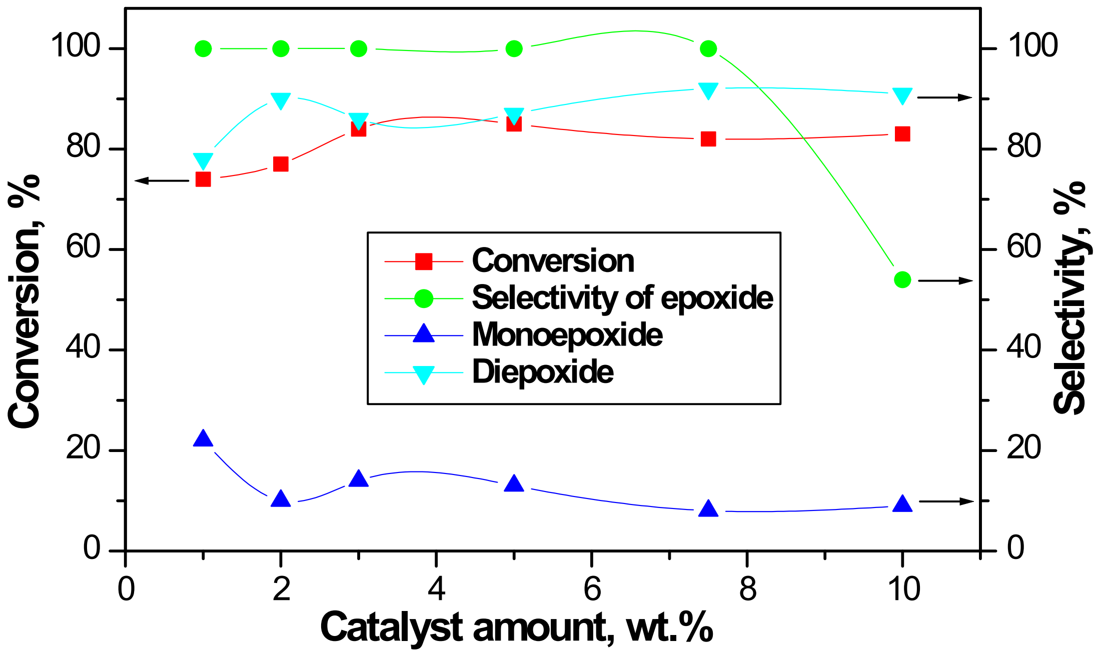


Fig. S5. Catalyst amount variation studies

TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Temp. = 110 °C, Time = 4 h

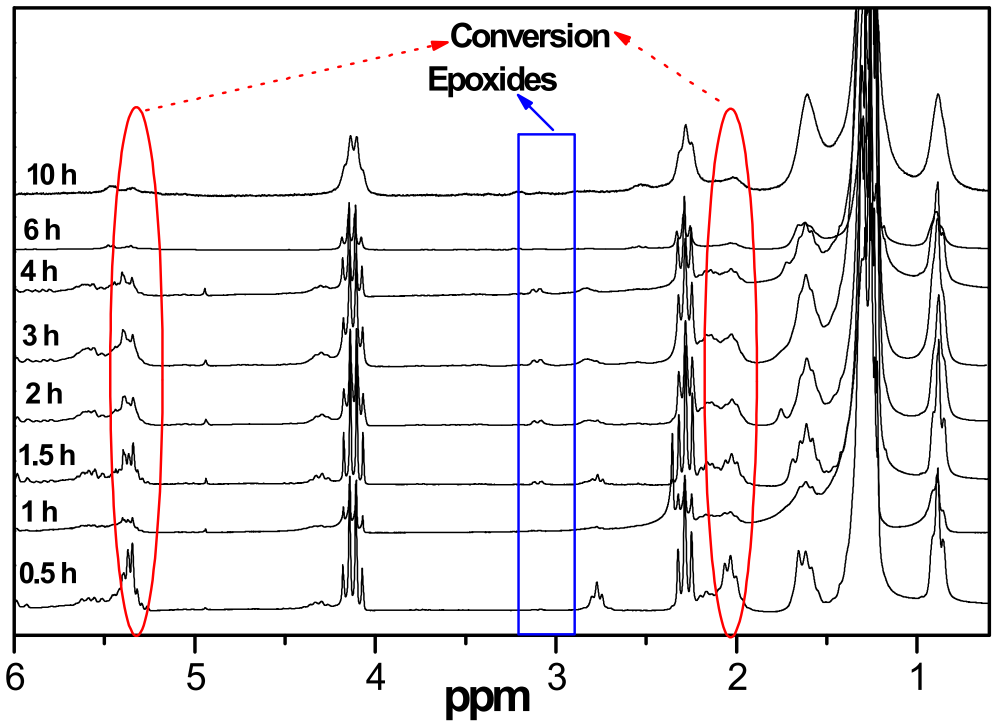


Fig. S6. Epoxidation of ethyl linoleate monitored at different time using [1]H NMR TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. ethyl linoleate), Temp. = 110 ºC

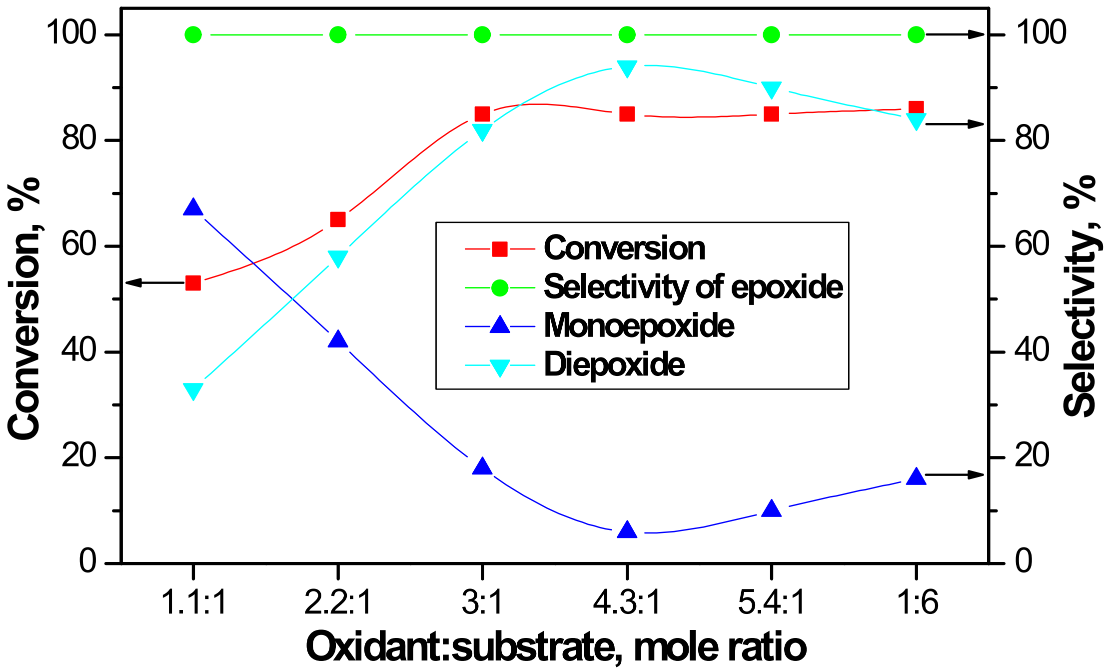


Fig. S7 Oxidant:substrate mole ratio variation studies

Ethyl linoleate =1 g, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}$Al-LDH (3 wt.% w.r.t. ethyl linoleate), Temp. = 110 °C , Time = 4 h

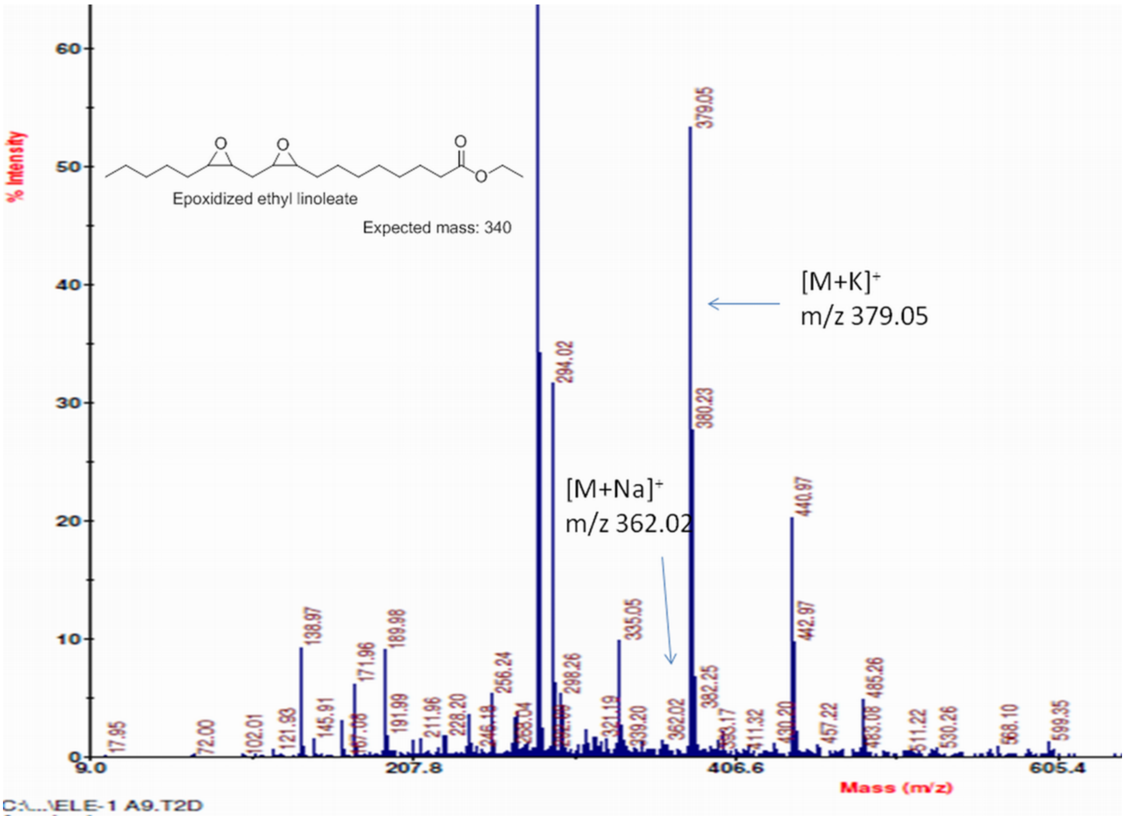


Fig. S8. MALDI-TOF analysis of epoxidized ethyl linoleate

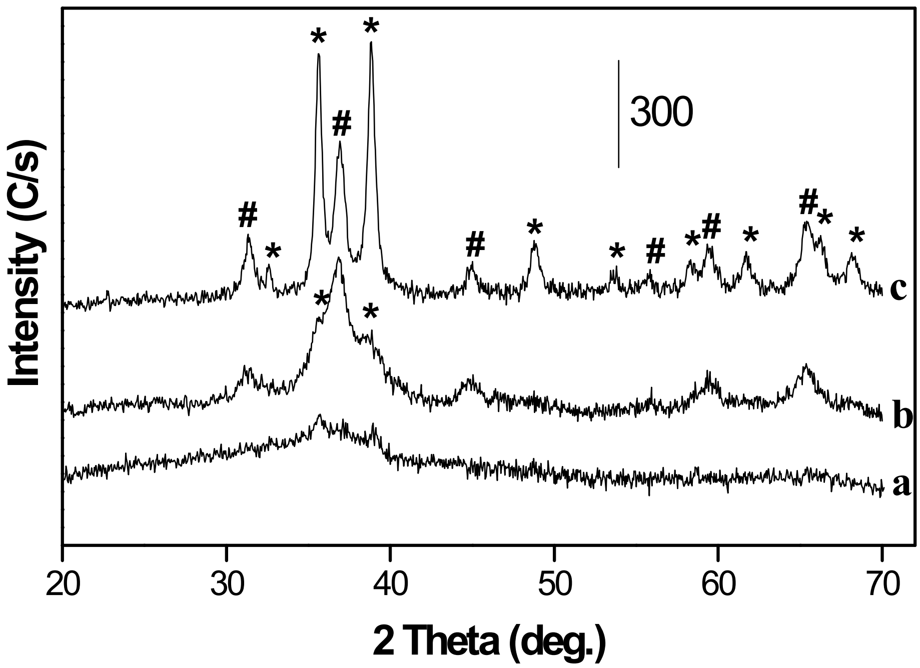


Fig. S9. PXRD patterns of (a) $Co_{30}Cu_{70}Al$-$CLDH_{300}$, (b) $Co_{30}Cu_{70}Al$-$CLDH_{500}$, (c) $Co_{30}Cu_{70}Al$- $CLDH_{700}$; $^{\#}$Spinel, *Tenorite (CuO; JCPDS: 00-045-0937)

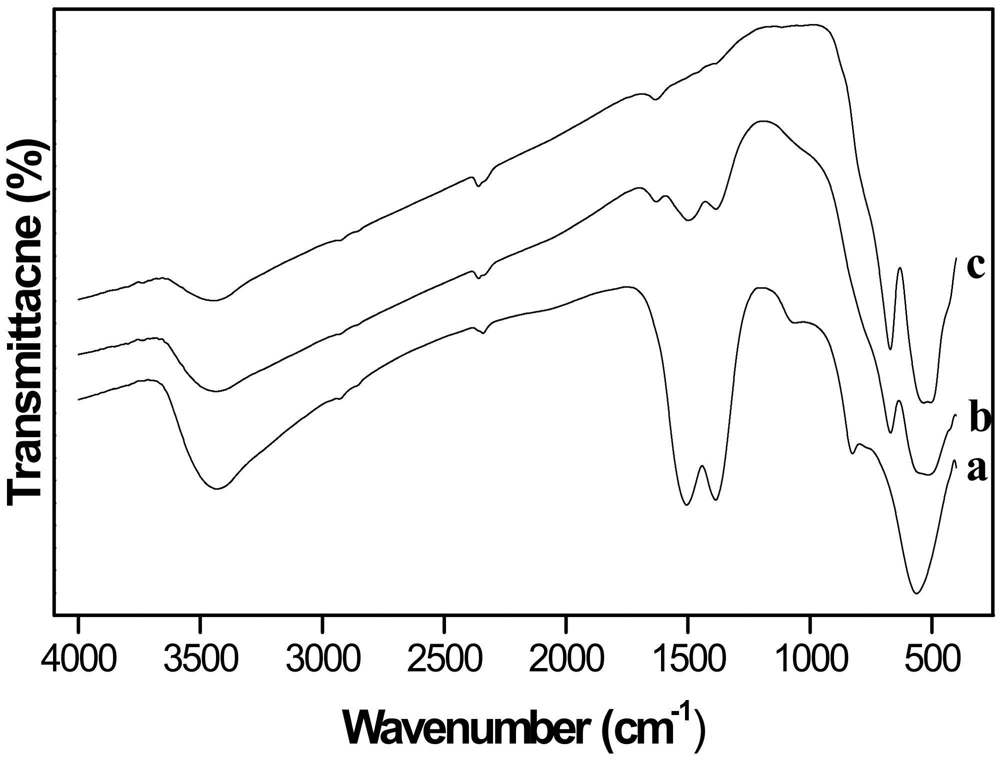


Fig. S10. FT-IR spectra of (a) $Co_{30}Cu_{70}Al$-$CLDH_{300}$, (b) $Co_{30}Cu_{70}Al$-$CLDH_{500}$, (c) $Co_{30}Cu_{70}Al$- $CLDH_{700}$

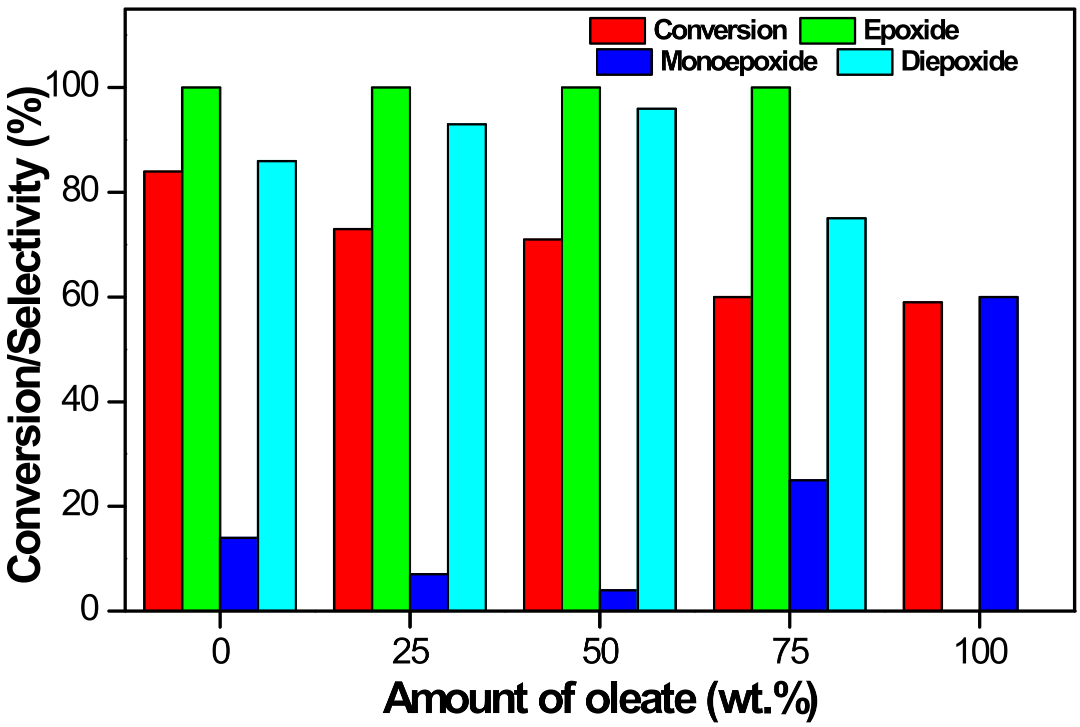


Fig. S11. Epoxidation of ethyl linoleate species in presence of methyl oleate
Ethyl linoleate & Methyl oleate = 1g, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. substrate), Temp. = 110 °C, Time = 4 h. (Faced difficulty in the quantification of epoxide selectivity while using 100 wt.% oleate as substrate)

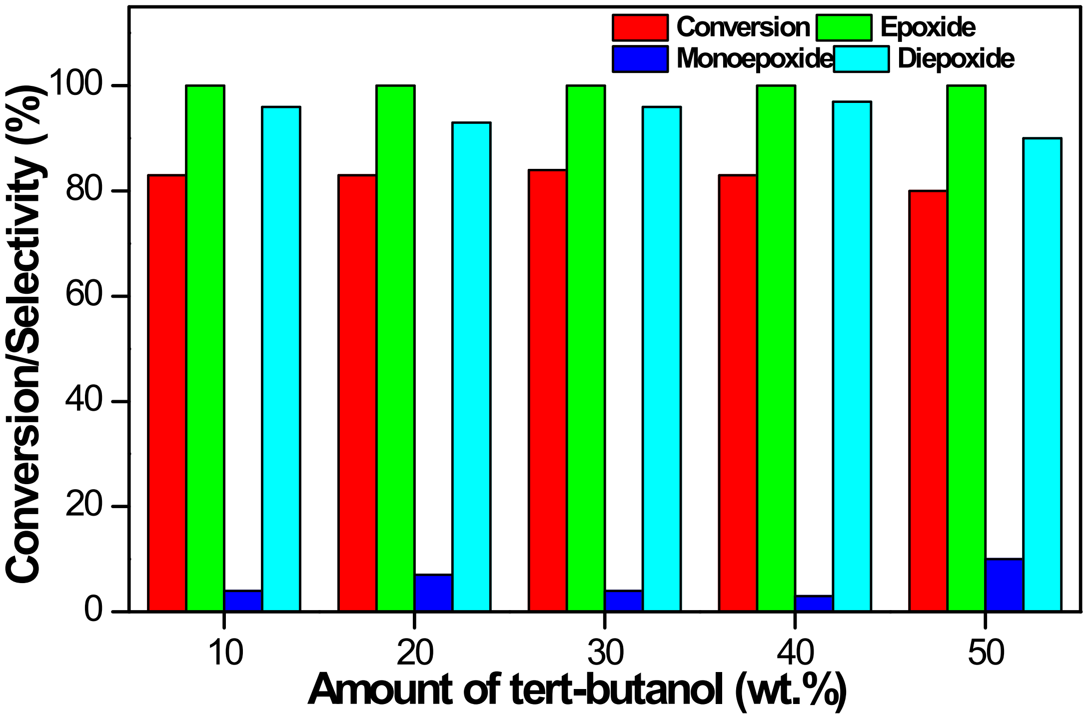


Fig. S12. Epoxidation of ethyl linoleate in presence of tert-butanol

Ethyl linoleate & *tert*-butanol = 1g Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. substrate), Temp. = 110 °C, Time = 4 h

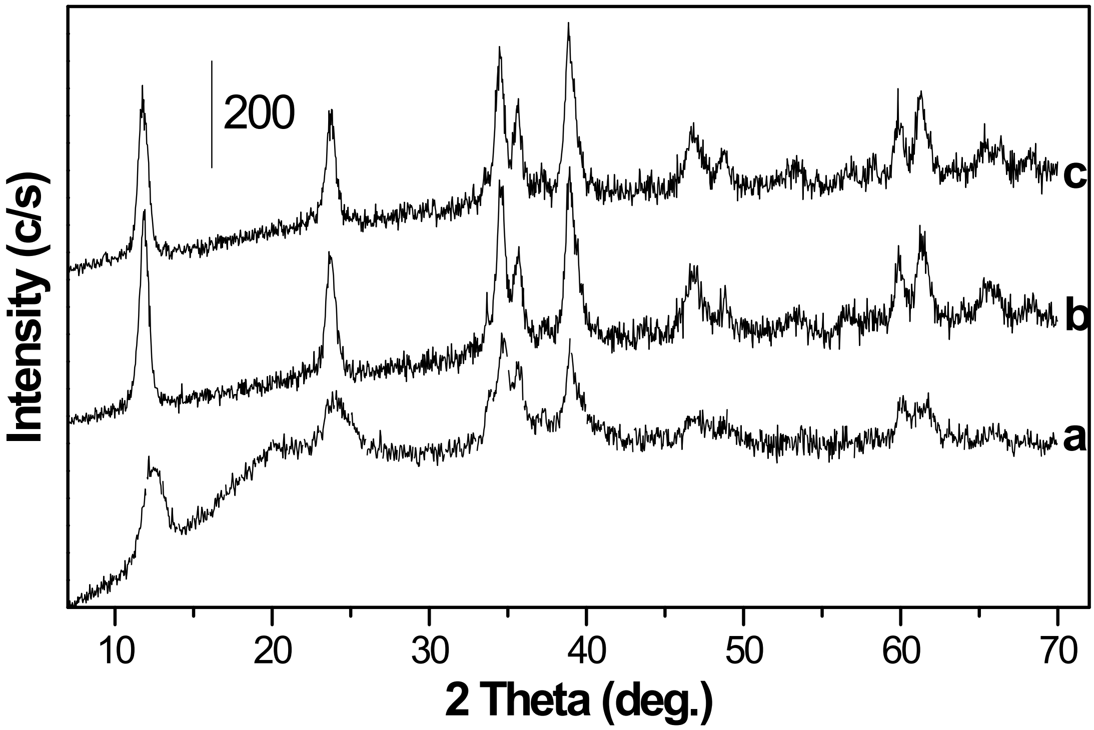


Fig. S13. PXRD patterns of (a) $Co_{30}Cu_{70}Al$-LDH, (b) catalyst ‘a’ after third cycle, (c) catalyst ‘a’ after sixth cycle

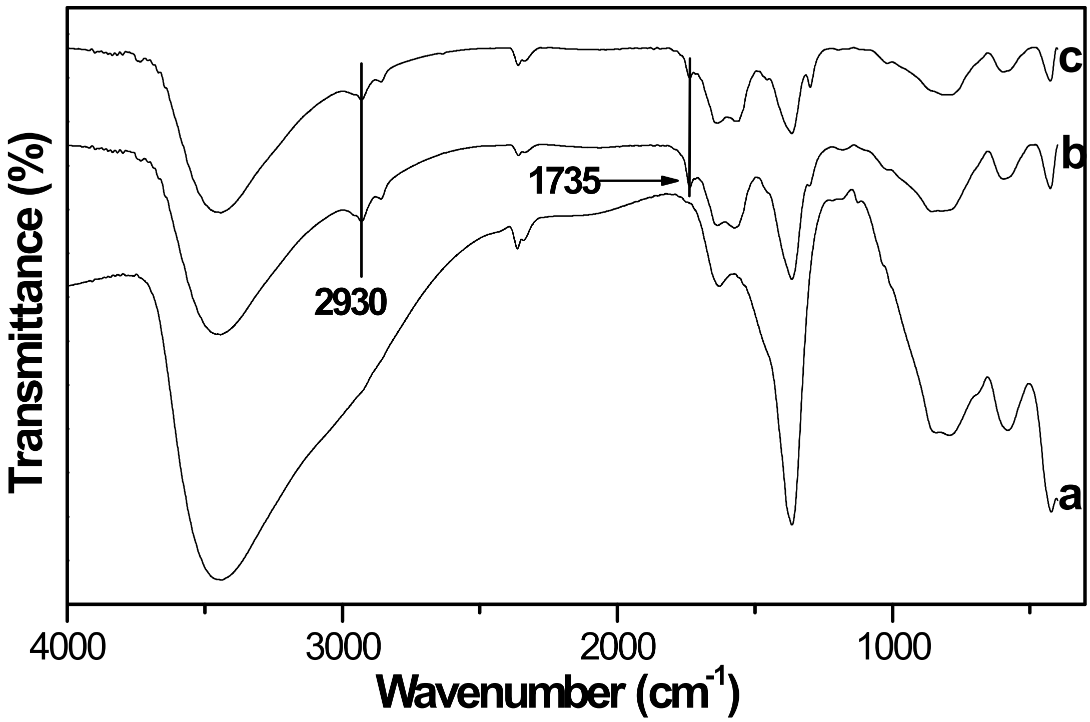


Fig. S14. FT-IR spectra of (a) $Co_{30}Cu_{70}Al$-LDH, (b) catalyst 'a' after third cycle, (c) catalyst 'a' after sixth cycle

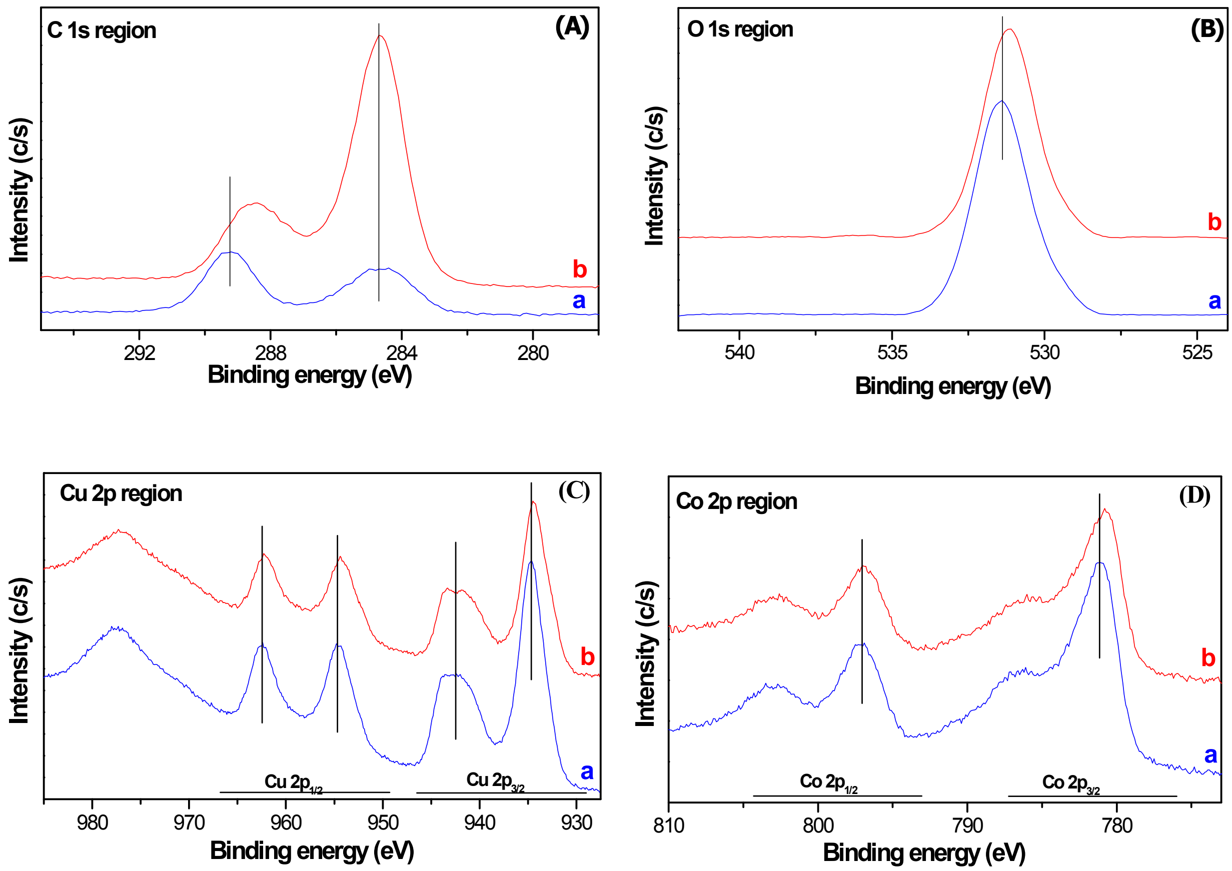
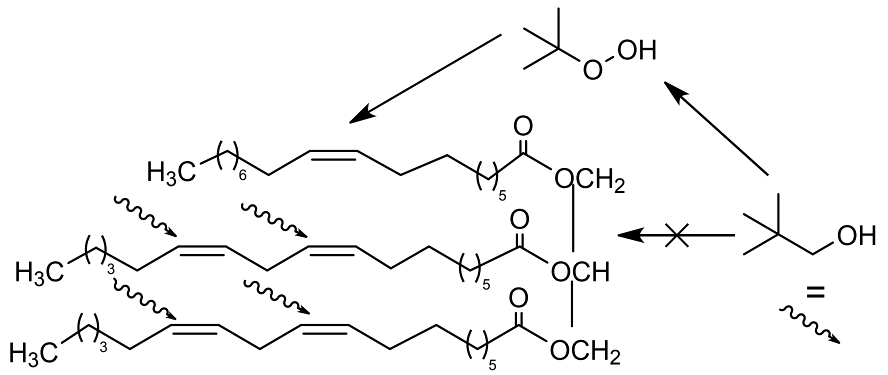
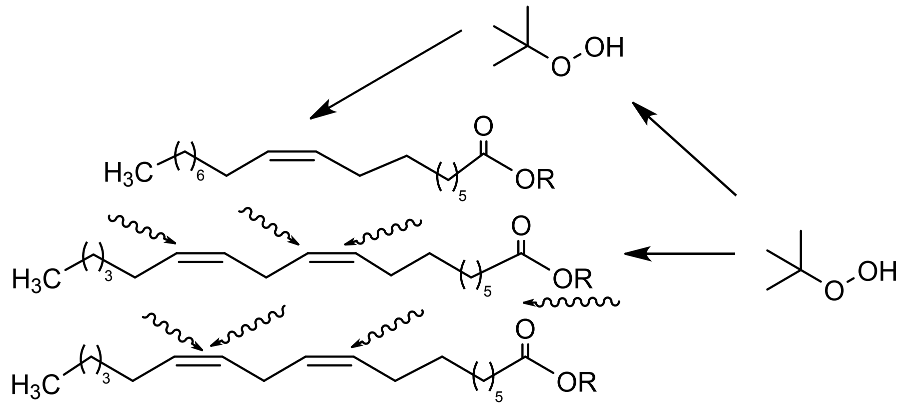


Fig. S15. (A) C 1s, (B) O 1s, (C) Cu 2p and (D) Co 2p XP spectra of (a) $Co_{30}Cu_{70}$Al-LDH and (b) catalyst 'a' after first cycle



Sunflower oil epoxidation



Sunflower FAME/ethyl linoleate epoxidation

Fig. S16. Mechanism of TBHP attack for the epoxidation of sunflower oil/(FAME) and ethyl linoleate

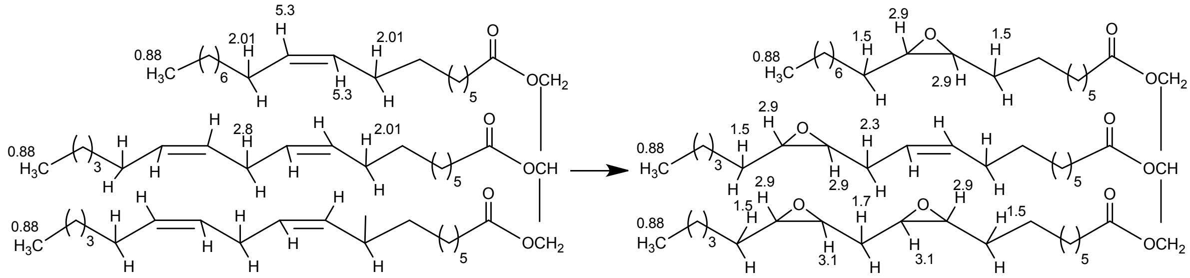


Fig. S17. Chemical shifts observed in ^{1}H NMR for oleate and linoleate groups of vegetable oil and its epoxidized derivatives

Table S1 Elemental chemical analysis, lattice parameters, empirical formula and colour of the materials synthesized

Material	Co/Cu[a]		(Co+Cu)/Al[a]		Lattice parameters		Empirical formula[b]	Colour
	Solution	Solid	Solution	Solid	a (Å)	c (Å)		
$Co_{100}Cu_0Al$-LDH	-	-	3.0	3.45	3.085	23.12	$[Co_{0.77}Cu_0Al_{0.23}(OH)_2](CO_3)_{0.11}.0.50H_2O$	Camel
$Co_{90}Cu_{10}Al$-LDH	9.0	7.10	3.0	2.91	3.076	23.02	$[Co_{0.66}Cu_{0.09}Al_{0.25}(OH)_2](CO_3)_{0.13}.0.83H_2O$	Burlywood
$Co_{70}Cu_{30}Al$-LDH	2.33	1.82	3.0	3.01	3.076	22.59	$[Co_{0.50}Cu_{0.25}Al_{0.25}(OH)_2](CO_3)_{0.12}.0.53H_2O$	Almond
$Co_{50}Cu_{50}Al$-LDH	1.0	0.76	3.0	3.21	3.083	22.78	$[Co_{0.34}Cu_{0.42}Al_{0.24}(OH)_2](CO_3)_{0.12}.0.68H_2O$	Bone
$Co_{30}Cu_{70}Al$-LDH	0.42	0.40	3.0	3.14	3.082	22.49	$[Co_{0.23}Cu_{0.53}Al_{0.24}(OH)_2](CO_3)_{0.12}.0.69H_2O$	Gray
$Co_{10}Cu_{90}Al$-LDH	0.11	0.09	3.0	3.39	3.082	22.51	$[Co_{0.07}Cu_{0.70}Al_{0.23}(OH)_2](CO_3)_{0.11}.0.85H_2O$	Sky blue

[a]Atomic ratio; [b]Values rounded to significant figure

Table S2 Surface atomic composition, binding energies, FWHM and intensity ratios of main and satellite peaks obtained through X-ray Photoelectron spectroscopy studies

Catalyst	Surface composition (atom%)[a]					Binding energies (FWHM) eV		I_s / I_m	
	Co	Cu	Al	Co/Cu	(Co+Cu)/Al	Co $2p_{3/2}$	Cu $2p_{3/2}$	Cu	Co
$Co_{100}Cu_0$Al-LDH	24.5	-	2.8	-	8.8	781.3 (2.3)	-	-	0.44
$Co_{50}Cu_{50}$Al-LDH	14.3	11.3	2.6	1.3	9.8	781.4 (1.8)	935.2 (2.7)	0.44	0.46
$Co_{30}Cu_{70}$Al-LDH	10.4	14.0	2.0	0.7	12.2	781.2 (2.7)	935.0 (3.2)	0.50	0.47
$Co_{10}Cu_{90}$Al-LDH	2.8	19.8	2.4	0.1	9.4	781.5 (2.7)	935.3 (2.7)	0.52	0.45

[a]Values rounded to significant figure

Table S3 Time variation studies [a]

Time (h)	Conversion (%)	Selectivity of epoxide (%)	Selectivity (%)	
			Monoepoxide	Diepoxide
0.5	56	100	81	19
1	64	100	51	49
1.5	75	100	27	73
2	77	100	18	82
3	79	100	21	79
4	84	100	14	86
6	83	62	40	60
10	84	61	40	60

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. ethyl linoleate), Temp. = 110 ºC

Table S4 Temperature variation studies [a]

Temperature (°C)	Conversion (%)	Selectivity of epoxide (%)	Selectivity (%)	
			Monoepoxide	Diepoxide
R.T.	40	100	100	0
60	44	100	79	21
85	68	100	39	61
110	84	100	14	86
125	81	100	6	94
140	81	100	11	89

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. ethyl linoleate), Time = 4 h

Table S5 Stirring speed variation studies[a]

Stirring speed (rpm)	Conversion (%)	Selectivity of epoxide (%)	Selectivity (%)	
			Monoepoxide	Diepoxide
100	74	100	18	82
300	82	100	11	89
700	83	100	12	88
1100	84	100	14	86

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}Al$-LDH (3 wt.% w.r.t. ethyl linoleate), Temp. = 110 ºC, Time = 4 h

Table S6 Oxidant variation studies

Entry No.	Oxidant[a]	Condition	Conversion (%)	Selectivity of epoxide (%)	Selectivity (%)	
					Monoepoxide	Diepoxide
1	H_2O_2	Atmospheric	19	100	100	0
2	Air[b]	Atmospheric	48	100	92	8
3	Oxygen[b]	Atmospheric	54	100	71	29
4	TBHP	N_2 atmosphere	79	100	12	88
5	TBHP	N_2 bubbling	81	100	6	94
6	TBHP	O_2 atmosphere	80	100	12	88
7	TBHP	O_2 bubbling[c]	82	100	50	50

[a]Oxidant:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = $Co_{30}Cu_{70}$Al-LDH (3 wt.% w.r.t. ethyl linoleate), Temp. = 110 °C, Time = 4 h; [b]bubbling condition; [c]Solvent evaporation was observed

Table S7 Textural properties and catalytic activities of $Co_{30}Cu_{70}Al$-LDH calcined at different temperatures

Catalyst[a]	**Surface area ($m^2 g^{-1}$)**	**Pore volume ($cm^3 g^{-1}$)**	**Conv. (%)**	**Selectivity of epoxide (%)**	**Selectivity (%)**	
					Monoepoxide	**Diepoxide**
$Co_{30}Cu_{70}Al$-$CLDH_{300}$	66	0.16	85	100	3	97
$Co_{30}Cu_{70}Al$-$CLDH_{500}$	65	0.15	80	100	2	98
$Co_{30}Cu_{70}Al$-$CLDH_{700}$	33	0.06	65	100	49	51

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = 3 wt.% w.r.t. ethyl linoleate, Temp. = 110 °C, Time = 4 h

Table S8 Reusability studies for $Co_{30}Cu_{70}Al$-$CLDH_{300}$ catalyst

Cycle[a]	**Conversion (%)**	**Selectivity of epoxide (%)**	**Selectivity (%)**	
			Monoepoxide	**Diepoxide**
Cycle - 1	85	100	2	98
Cycle - 2	84	100	2	98
Cycle - 3	83	100	2	98

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = 3 wt.% w.r.t. ethyl linoleate, Temp. = 110 °C, Time = 4 h

Table S9 Catalytic activities of different catalysts for the preparation of fatty epoxides

Catalyst[a]	**Name of the Reactant**	**Time (h)**	**Temp. (°C)**	**Conv. (%)**	**Selectivity of epoxide (%)**	**Selectivity (%)**		**Reference**
						Monoepoxide	**Diepoxide**	
$Co_{30}Cu_{70}$Al-LDH	Ethyl linoleate	4	110	84	100	14	86	This work
Basic alumina	Ethyl linoleate	4	110	25	100	100	0	This work
Acidic alumina	Ethyl linoleate	4	110	27	100	75	25	This work
Neutral alumina	Ethyl linoleate	4	110	18	100	94	6	This work
Basic alumina[b]	Ethyl linoleate	4	110	33	100	98	2	This work
Acidic alumina[b]	Ethyl linoleate	4	110	20	100	81	19	This work
Neutral alumina[b]	Ethyl linoleate	4	110	45	100	73	27	This work
MgAl-LDH	Ethyl linoleate	4	110	31	100	100	0	This work
NiAl-LDH	Ethyl linoleate	4	110	30	100	94	6	This work
$Co_{30}Mg_{70}$Al-LDH	Ethyl linoleate	4	110	80	83	8	92	This work
$Co_{30}Ni_{70}$Al-LDH	Ethyl linoleate	4	110	79	82	12	88	This work
$Co_{30}Mn_{70}$Al-LDH	Ethyl linoleate	4	110	79	73	12	88	This work
$Co_{30}Cu_{70}$Al-LDH[c]	Sunflower oil	4	110	69	100	10	90	This work
$Co_{30}Cu_{70}$Al-LDH[d]	Soybean oil	4	110	69	100	12	88	This work
$Co_{30}Cu_{70}$Al-LDH[e]	Jatropha oil	4	110	70	100	44	56	This work
$Co_{30}Cu_{70}$Al-LDH[f]	Castor oil	4	110	40	100	98	2	This work
$Co_{30}Cu_{70}$Al-LDH[g]	Sunflower FAME	4	110	78	100	6	94	This work

Ti/SiO_2 [h]	Soybean oil	54	90	89[m]	-	-	-	[25]
Ti/MCM-41 [i]	Oleate rich sunflower FAME	24	90	98	85	-	-	[26]
Ti/MCM-41 [h]	Methyl oleate	24	85	96	95	-	-	[27]
Immobilized lipase [h]	Jatropha methyl esters	24	25	100	100	-	-	[28]
Amberlite-IR 120 [h]	Jatropha methyl esters	24	57	90	70	-	-	[28]
Molybdenum (VI) complex [j]	Soybean oil	2	110	70	77	-	-	[29]
molybdenum acetylacetonate immobilized on clay [k]	Castor oil	24	80	100	58	-	-	[30]
molybdenum acetylacetonate immobilized on clay [k]	Soybean oil	24	80	100	39	-	-	[30]
15% $MoOx/Al_2O_3$	Soybean methyl esters	6	100	90	-	-	-	[31]

[a]TBHP:Ethyl linoleate = 3:1 mole ratio, Toluene = 2 ml, Catalyst = 3 wt.% w.r.t. ethyl linoleate, Temp. = 110 ºC, Time = 4 h; [b]Activated at 500 °C/5 h, [c] TBHP: Oil = 8.8:1 mole ratio, [d]TBHP: Oil = 7.6:1 mole ratio, [e]TBHP: Oil = 7.2:1 mole ratio, [f]TBHP: Oil = 7.7:1 mole ratio, [g]TBHP:Oil = 2.9:1 mole ratio, [h]H_2O_2 as oxidant, [i]TBHP:FAME = 1.33 mole ratio, [j]Homogeneus system, [k]TBHP: double bond = 4:1 mole ratio, [l]TBHP:double bond = 1.5:1 mole ratio, [m]88% yield of epoxidized oil

Table S10 Characteristic properties of vegetable oils

	Name of the vegetable oil	Acid value (mg KOH/g)	FFA (A.V./2)	Average mol. wt.	Fatty acids (%)[a]					Double bonds/mol[29]
					Saturated		Unsaturated		Others	
					Palmitic (*16:0*)	Stearic (*18:0*)	Oleic (*18:1*)	Linoleic (*18:2*)		
Edible oils	Sunflower oil	0.47	0.235	899	15	11	13	55	6	4.40
	Groundnut oil	4.49	2.245	782	19	9	10	48	14	3.28
	Gingelly oil	3.93	1.965	780	16	13	16	53	2	3.44
	Soyabean oil	0.56	0.280	774	18	8	11	61	2	4.60
	Cottonseed oil	0.56	0.280	803	29	6	10	50	5	3.46
	Corn oil	0.56	0.280	785	23	6	10	58	3	3.86
	Rice bran oil	2.81	1.405	788	25	3	18	50	4	3.34
Non-edible oils	Jatropha curcus oil	30.82	15.410	736	19	11	19	50	1	2.96
	Pinnai oil	20.76	10.380	789	22	13	18	42	5	2.48

	Karingatta oil	22.44	11.220	827	19	15	12	53	1	3.76
	Castor oil[b]	3.93	1.965	810	2	2	4	6	86	1.24
Used cooking oils	Once cooked (sunflower) oil	1.40	0.700	723	10	5	11	71	3	4.38
	Doubly cooked (sunflower) oil	2.16	1.080	634	12	10	17	58	3	4.90
	Waste cooked (cottonseed) oil	1.12	0.560	694	33	3	10	51	3	2.88

[a](xx:y - No. of carbon atoms:unsaturated centers); [b]Ricinoleic acid (18:1) - 86%