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Electronic Supplementary Information

# Selective liquid phase benzyl alcohol oxidation over Cu-loaded $LaFeO_3$ perovskite

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**Table S1** Benzyl alcohol oxidation activities of different copper loaded CuXLaM perovskites[a]

| Name | Conversion (%) | Products (%)[b] | | Benzaldehyde Selectivity (%) | TON[c] |
|---|---|---|---|---|---|
| | | A | B | | |
| Cu5LaMn | 56.3 | 55.6 | 0.7 | 98.7 | 543 |
| Cu10LaMn | 82.3 | 81.7 | 0.6 | 99.3 | 399 |
| Cu5LaFe | 75.4 | 75.4 | 0 | 100 | 739 |
| Cu10LaFe | 98.7 | 98.7 | 0 | 100 | 481 |
| Cu5LaCo | 50.7 | 49.6 | 1.1 | 97.8 | 502 |
| Cu10LaCo | 78.3 | 73.6 | 4.7 | 94.0 | 386 |
| Cu10LaFeIWI | 83.1 | 78.9 | 4.2 | 94.9 | 405 |

[a] Reaction condition: 0.05 g catalyst, 1 mL benzyl alcohol, 10 mL MeCN, 2.75 mL TBHP, 80 °C, 3 h.

[b] A= Benzaldehyde and B= Benzyl benzoate (byproduct).

[c] Turnover Number (TON) = Moles of benzyl alcohol converted per mole of copper taken in synthesis (nominal value).

## Effects of TBHP concentration and its decomposition

An iodometric titration is used to determine the amount of TBHP consumed for the benzyl alcohol oxidation. The conversion (Conv) and the selectivity (SE) of TBHP in mol % are defined as follows.

$$\text{Conv} = \frac{\text{consumption of TBHP }\left(\text{including self decomposition}\right)}{\text{initial amount of TBHP}}$$

$$\text{SE} = \frac{\text{TBHP consumption for benzyl alcohol formation}}{\text{total consumption of TBHP}}$$

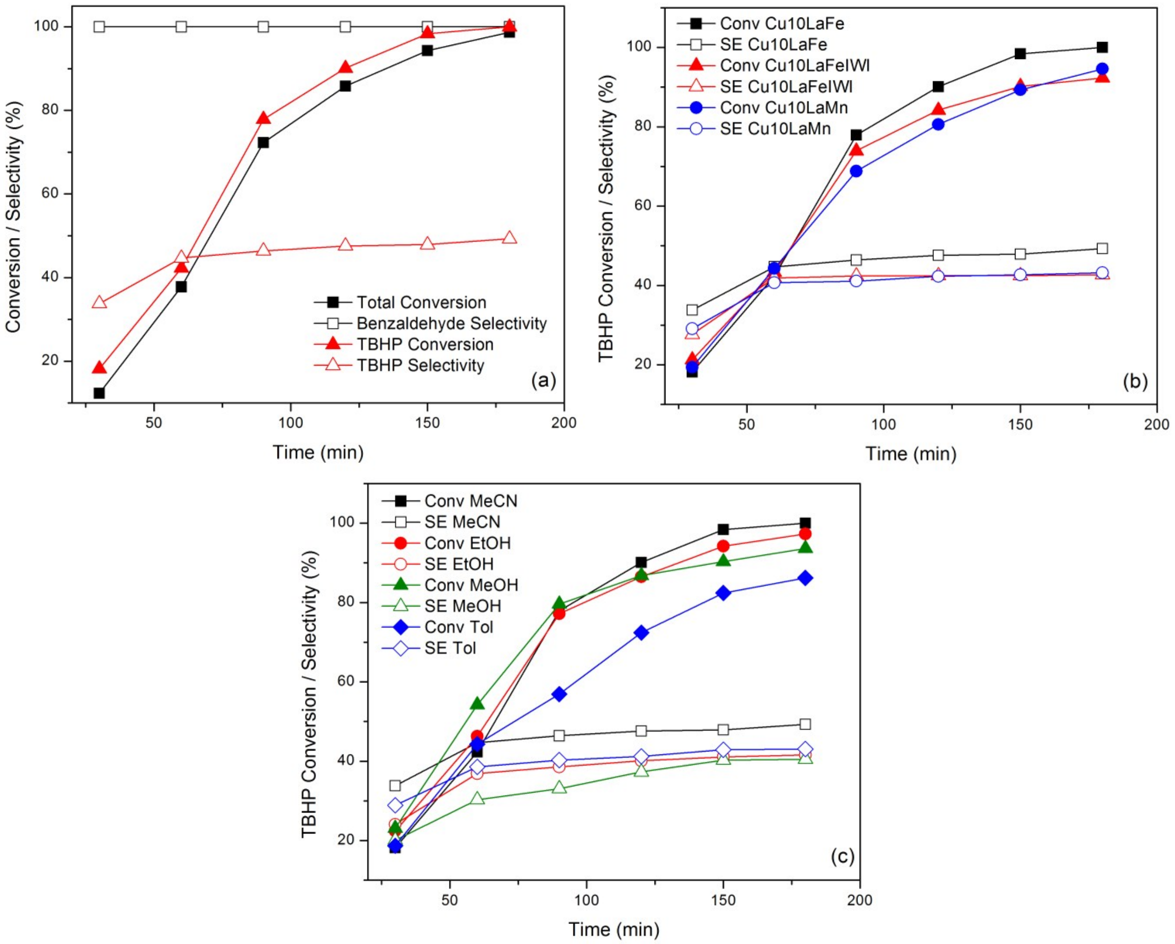

**Fig. S1.** Time variation of (a) benzyl alcohol conversion, benzaldehyde selectivity, TBHP conversion (Conv) and the corresponding selective decomposition (SE) observed over Cu10LaFe (solvent is MeCN), (b) TBHP Conv and SE over Cu10LaFe, Cu10LaFeIWI and Cu10LaMn catalysts (solvent is MeCN) and (c) TBHP Conv and SE in different solvents, MeCN, EtOH, MeOH and toluene (Tol). Other reaction conditions: 0.05 g catalyst, 1 mL benzyl alcohol, 10 mL solvent, 2.75 mL TBHP and 80 °C (all under reflux).

It is to be noted that the higher the percentage of TBHP decomposition during the entire course of oxidation, the higher will be the benzyl alcohol conversion but an initial high value of TBHP decomposition will lead to a nonselective decomposition of TBHP. A high percentage of TBHP decomposition associated with a low initial rate of decomposition favours the effective utilization of TBHP as an oxidant and it thus enhances the rate of oxidation reaction [15, 23, 32].

The time dependence of TBHP conversion together with the benzyl alcohol conversion over Cu10LaFe shows similar trends– reaching the maximum after 3 h of reaction (see **Fig. S1(a)**). Benzaldehyde is formed as the exclusive product with 100 % selectivity. But the TBHP selectivity maintains an initial low value (~34 mol % at 30 min) owing to its unavoidable self decomposition that is increased to ~45 mol % after 1 h and it is increased only a little (up to ~49 mol %) even after 3 h of reaction (see **Fig. S1(a)**).

**Fig. S1(b)** represents the TBHP conversion and selectivity values over the combustion synthesized Cu10LaFe; it's analogous impregnated catalyst Cu10LaFeIWI; together with those over combustion synthesized Cu10LaMn that has shown the second highest benzyl alcohol oxidation behaviour. The highest (~49 mol %) TBHP selective decomposition is noted over the Cu10LaFe catalyst when compared with the other two (~43 mol % for both the Cu10LaFeIWI and Cu10LaMn catalysts). These data clearly suggest that the Cu10LaFe catalyst utilizes the oxidant most effectively which is reflected in the benzyl alcohol conversion as well as the benzaldehyde selectivity values observed over these three formulations.

We have shown that there are certain effects of the four solvents on the benzyl alcohol oxidation behaviour, but these are not so dramatic. Acetonitrile indeed shows the minimum TBHP conversion (18.2 mol %) after 30 min of reaction and it is completed after 3 h of reaction (see **Fig. S1(c)**). The TBHP conversion over ethanol and methanol are comparatively lower and toluene shows the lowest conversion. This is also the benzyl alcohol conversion order of Cu10LaFe catalyst in different solvents. Note that the order of initial (30 min) TBHP conversion is: acetonitrile (18.2 mol %) ≈ toluene (18.7 mol %) < ethanol (22.4 mol %) ≈ methanol (23.1 mol %). The selective decomposition of TBHP and thus the benzaldehyde selectivity follows the same trend.

The highest peroxide selectivity in acetonitrile than in the other solvents can account for the highest benzyl alcohol conversion as well as benzaldehyde selectivity in it. Although the TBHP selective decomposition is comparable in ethanol, methanol and toluene, the conversion of TBHP is relatively higher in the alcohols than in toluene. Decomposition of TBHP is more in the polar solvents than in the nonpolar solvent toluene. In the polar protic solvents, the generated peroxide radical gets additional stability due to the H-bond formation and the equilibrium is shifted towards the right thereby increasing the rate of self decomposition. Thus, the loss of TBHP due to self decomposition is more during initial stages in ethanol and methanol. The fraction of peroxide radical utilized for benzaldehyde formation is thus less compared to the total TBHP decomposition in these solvents. As expected, the nonpolar aprotic solvent toluene shows the lowest TBHP conversion but a comparable peroxide selectivity to ethanol owing to its low self decomposition. Because of the polar aprotic character of acetonitrile, the generated peroxide radical does not get additional stability in it as in the polar protic solvents; eventually reducing the self decomposition of TBHP. The best oxidation behavior is thus observed in acetonitrile.

## Sheldon test and mechanistic aspects

In order to see whether the present perovskite catalyst is functioning in a truly heterogeneous manner, the conventional hot filtration test of Sheldon is carried out. For this, the catalyst is immediately filtered off from the hot reaction mixture through a Gooch (G4) after 1 h of oxidation at 80 °C in order to avoid re-adsorption of the leached metals, if any, onto the catalyst surface. The filtrate is collected into another preheated round bottom flask maintained at the same temperature and the reaction is continued for another 2 h. The gas chromatographic analysis of the reaction aliquot shows a constant conversion of 38 % up to 3 h for the combustion synthesized catalyst Cu10LaFe when compared with the time variation of the activity pattern of this catalyst (see **Fig. S2(a)**). But for the Cu10LaFeIWI catalyst, the hot filtration test shows although little but certain increase in the conversion (from 36.4 % to 44.2 %) during the studied timeframe (see **Fig. S2(a)**). The reaction is, therefore, truly heterogeneous in nature over the combustion synthesized Cu10LaFe catalyst and the possibility of metal leaching or decomposition of the catalyst material can be excluded. The certain improvement in the conversion even in the absence of catalyst for the Cu10LaFeIWI catalyst confirms that the benzyl alcohol oxidation over this impregnated catalyst is not purely heterogeneous in nature and there is a certain amount of leaching of the active metal component to the solution during the progress of the reaction. We could not perform the Cu-analysis of the reaction crude after catalyst separation by the ICP-OES which could have shed more light towards our understanding of the leaching phenomenon.

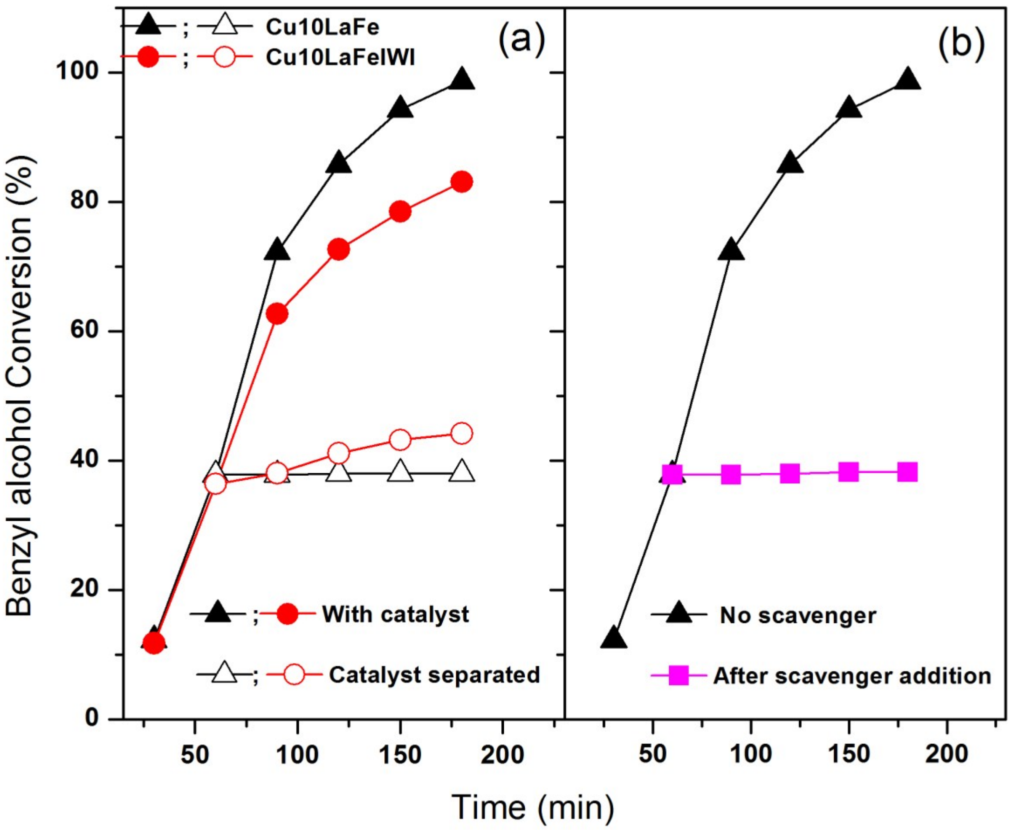

**Fig. S2** Benzyl alcohol conversion as a function of time (a) over Cu10LaFe and Cu10LaFeIWI and after removal of these catalysts from the reaction mixture (Sheldon's test) after 1 h and (b) over Cu10LaFe and after addition of scavenger (quinone) after 1 h at 80 °C (all under reflux).

The above findings imply that the $Cu^{2+}$ ion sites on the LaFe perovskite are stable enough (do not leach out to the solution phase) towards the oxidation reaction for the combustion synthesized catalyst (Cu10LaFe) and hence the oxidation activity of this material remains essentially same in the consecutive catalytic cycles. Whereas, the finely dispersed CuO crystallites in the impregnated catalyst (Cu10LaFeIWI) can grow bigger/ agglomerate with the progress of reaction. These larger crystallites can escape from the surface of the catalyst during the oxidation process in the successive cycles resulting in consecutively lower activity in the various oxidation cycles of benzyl alcohol.

The oxidation of benzyl alcohol over one-electron oxidant like copper generally proceeds through a radical pathway in presence of a peroxide oxidant [27]. In order to investigate the oxidation mechanism involved in the present case, we have performed the reaction in the presence of quinone, a radical scavenger. The scavenger was added to the reaction mixture after 1 h of oxidation and the progress of the reaction was monitored in the usual manner. The analysis of the reaction aliquot clearly shows that the benzyl alcohol oxidation is totally stopped after the addition of the scavenger (see **Fig. S2(b)**). We thus believe that the oxidation process proceeds through a radical mechanism over the perovskite catalyst reported in this study having similarity with previous literature reports [24, 27, 28]. To specify further, the metal ion (here copper) acts as an initiator of the free radical auto oxidation processes by promoting the decomposition of alkyl hydroperoxides (like TBHP in this study) in to chain initiating alkylperoxy (tertiarybutylperoxy) radicals mediated via the involvement of $Cu^{2+} \leftrightarrow Cu^{+}$ redox couple (one-electron transfer process promoted by $LaFeO_3$ perovskite) that subsequently abstracts hydrogen (by homolytic cleavage) from the reactant (benzyl alcohol) to produce benzylhydroxy free radical and TBHP. This radical eventually reacts further with the tertiarybutylperoxy radical to form benzaldehyde and tertiary butanol. The benzylhydroxy free radical may further react with benzaldehyde to form the side product benzylbenzoate. A plausible mechanistic scheme can be as follows:

$(CH_3)_3COOH$ + Cu-cat $\rightarrow$ $(CH_3)_3CO^{\cdot}$ + $^{\cdot}OH$ (Self decomposition)

$(CH_3)_3COOH$ + Cu-cat $\rightarrow$ $(CH_3)_3COO^{\cdot}$ +$H^{\cdot}$

$^{\cdot}OH$ + $(CH_3)_3COOH$ $\rightarrow$ $H_2O$ + $(CH_3)_3COO^{\cdot}$ (Self decomposition)

$(CH_3)_3CO^{\cdot}$ + $(CH_3)_3COOH$ $\rightarrow$ $(CH_3)_3COH$+ $(CH_3)_3COO^{\cdot}$ (Self decomposition)

$(CH_3)_3COO^{\cdot}$ +$ArCH_2OH$ $\rightarrow$ $ArCH^{\cdot}-OH$ + $(CH_3)_3COOH$

$(CH_3)_3CO^{\cdot}$ + $ArCH_2OH$ $\rightarrow$ $(CH_3)_3COH$+ $ArCH^{\cdot}-OH$

$ArCH^{\cdot}-OH$ + $(CH_3)_3COO^{\cdot}$ $\rightarrow$ ArCHO + $(CH_3)_3COOH$

$ArCH^{\cdot}-OH$ $\rightarrow$ ArCHO +$H^{\cdot}$

$ArCH^{\cdot}-OH$ + ArCHO $\rightarrow$ $ArCOOCH_2Ar$ + $H^{\cdot}$

$H^{\cdot}$ + $(CH_3)_3COOH$ $\rightarrow$ $(CH_3)_3COH$ + $H_2O$

(Cu-cat= copper loaded $LaFeO_3$ perovskite catalyst)

**Table S2** XPS core-level binding energies of Fe 2p$_{3/2}$, Cu 2p$_{3/2}$, La 3d$_{5/2}$, surface atomic composition and ratios of different catalysts

| Catalyst | Peak details | BE (eV) | % At conc | Cu/La | Fe/La | Cu/Fe | (Cu+Fe)/La |
|---|---|---|---|---|---|---|---|
| Cu10LaFe | Fe 2p$_{3/2}$ | 710.2 | 45.3 | 0.21 | 1.00 | 0.21 | 1.21 |
| | Cu 2p$_{3/2}$ | 932.8 | 9.3 | | | | |
| | La 3d$_{5/2}$ | 834.3 | 45.3 | | | | |
| Cu10LaFeCy2 | Fe 2p$_{3/2}$ | 710.3 | 42.6 | 0.17 | 0.87 | 0.20 | 1.05 |
| | Cu 2p$_{3/2}$ | 933.5 | 8.5 | | | | |
| | La 3d$_{5/2}$ | 834.6 | 48.9 | | | | |
| Cu10LaFeIWI | Fe 2p$_{3/2}$ | 710.8 | 41.0 | 0.21 | 0.84 | 0.25 | 1.05 |
| | Cu 2p$_{3/2}$ | 933.8 | 10.2 | | | | |
| | La 3d$_{5/2}$ | 834.7 | 48.8 | | | | |