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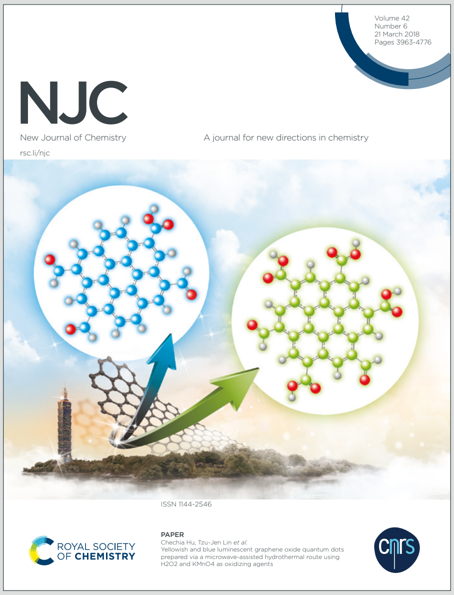

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A green approach for aerobic oxidation of benzylic alcohols catalysed by Cu^I-Y zeolite / TEMPO in ethanol without additional additives

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Abstract: An efficient and green protocol for aerobic oxidation of benzylic alcohols in ethanol using Cu^I-Y zeolite catalyst assisted with TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidine-N-oxyl) as the radical co-catalyst in presence of atmospheric air under mild conditions was reported. The Cu^I-Y zeolite prepared *via* ion exchange between CuCl and HY zeolite was fully characterized by a variety of spectroscopic techniques such as XRD, XPS, SEM, EDX and HRTEM. The incorporation of Cu(I) into the 3D-framework of the zeolite rendered the catalyst good durability. The results of repetitive runs revealed that in the first three-run, there was hardly decline in activity and more substantial decrease in yield was observed afterwards while selectivity remained almost unchanged. The loss in activity was attributed to both the formation of CuO and the bleaching of copper into the liquid phase during the catalysis, of which the formation of CuO was believed to be the major contributor since the bleaching loss for each run was neglectable (< 2%). In this catalytic system, except TEMPO, no other additives were needed, either a base or a ligand which had been essential in some reported catalytic systems for the oxidation of alcohols. The aerobic oxidation proceeded under mild conditions (60 ^oC, 18 hrs) to quantitatively and selectively convert a wide range of benzylic alcohols to corresponding aldehydes, which shows a great potential in developing green and environmentally benign catalysts for aerobic oxidation of alcohols. The system demonstrated excellent tolerance against electron-withdrawing group on the phenyl ring of the alcohols and showed sensitivity to steric hindrance of the substrates which is due to the confinement of the pores of the zeolite in which the oxidation occurred. Based on the mechanism reported in literatures for homogenous oxidation, a mechanism was analogously proposed for the aerobic oxidation of benzylic alcohols catalysed by this Cu(I)-containing zeolite catalyst.

1. Introduction

There has been an increasing demand in production of a variety of fine chemicals using efficient and environmentally benign processes in industries. One of such productions is the selective oxidation of alcohols to aldehydes since aldehydes are important precursors in various industries, for example, agrochemicals, pharmaceutics, fragrances.[1] Despite great efforts being put into this area, pursuing approaches with greener nature, better selectivity and milder reaction conditions remain one of the intensively studied areas and catalytic systems based on a variety of transition-metals including noble metals have been investigated to achieve high yield and better selectivity.[2-4] Of the transition metals employed in the catalysis, copper is of particular importance due to its good activity. This is not surprising since in nature, this metal is employed as the same function as showed in the copper-enzyme galactose oxidase which catalyses the aerobic oxidation of primary alcohols to aldehydes in biological systems.[5] Indeed, many homogeneous catalytic systems based on copper have been explored.[6-15] Despite the progress, how to develop a green and sustainable approach for the oxidation remains challenging, for example, catalyst reusability and green reaction media. Therefore, it is still highly desirable to develop novel strategy for the oxidation to take on the challenges.

To some extent, heterogeneous systems are of advantages in terms of recycling although catalytic activity may be compromised compared to homogenous systems under similar conditions. Indeed, a wide range of heterogeneous supports were utilised for supporting catalysts which have been proved effective in homogenous catalysis. For example, catalysts based on Cu(I)/TEMPO is such a system incorporated into a variety of materials, such as polymers,[16-18] metal oxides,[19, 20] polyoxometalates (POM),[21] metal organic frameworks (MOF),[22-24] silicates[25] and carbon[26, 27] materials. In developing such heterogeneous systems, minimising additional additives, for example, avoiding the use of a base, have been among the major considerations. In this regard, there have been some reports in the literatures, for example, Cu-Mn oxides / TEMPO for the aerobic oxidation of primary alcohols to aldehydes in chlorinated solvent,[28]

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sulfonated Cu(II)@$Cu_3(BTC)_2$ / TEMPO for the aerobic oxidation of benzylic alcohols without involving a base under mild conditions,[29] mixed valent Cu(I/II) nanoparticles immobilised on aminopropyl-functionalized controlled pore glass with TEMPO as the co-catalyst for the aerobic oxidation of alcohols under solvent-free conditions.[30] It was turned out that this system was applicable to a wide range of alcohol substrates. These heterogeneous catalysts have been proven effective and however, they were not ideal if the principle of green chemistry is considered.

Zeolites are important aluminosilicate family of materials with wide range of applications, for example, adsorption, gas separation, hydrocarbon cracking and organic syntheses.[31-34] This is mainly due to that zeolite possesses unique properties such as bifunctional acid-base nature, shape selectivity and high thermal stability. These advantages make zeolites excellent platforms to support transition metal catalysts for organic reactions.[35, 36] Recently, there were some reports showing that the Cu^I-exchanged zeolites were employed as a versatile catalyst for various organic reactions such as photochemical, cycloaddition and click reactions.[37-41] In the Cu^I-exchanged zeolite, the oxygen atoms of the zeolite framework act as the ligand to anchor and stabilise the metal ion.[42] It has been reported that the incorporation of copper in various types of zeolites to form Cu-clusters (dinuclear mono- and bis-(μ-oxo) core Cu clusters and μ-peroxo dicopper or trinuclear μ-oxo clusters) which resembled the active sites of some copper-containing enzymes, for example, particulate methane monooxygenase (pMMO) that catalyses aerobic oxidation of methane into methanol under physiological conditions.[43, 44] Incorporating noble metals into zeolite let to a catalyst effective on aerobic oxidation of benzylic alcohols.[45, 46] By considering the importance of copper in the catalysis of alcohols and the advantages of the Cu^I-Y zeolite in heterogeneity, it would be inspiring to examine the function of the Cu^I-Y zeolite in aerobic oxidation of alcohols. Herein, we report the catalysis of Cu^I-Y zeolite assisted with TEMPO as the radical co-catalyst in ethanol under mild conditions on the aerobic oxidation of benzylic alcohols. Our results showed that this approach converted selectively and quantitatively benzylic alcohols into aldehydes *via* aerobic oxidation and possessed excellent robustness and recyclability. The employment of ethanol as the reaction medium also demonstrated its eco-friendly characteristic. Furthermore, unlike our recent reported Cu_2O-based system for the same oxidation reaction, in which a ligand N-methylimidazole was required,[47] this system does not require any additional ligand and base.

2. Results and Discussion

2.1 Catalyst preparation and characterization

The Cu^I-Y zeolite was prepared according to the procedure reported using solid state vapour phase ion exchanged method.[42] A mixture of CuCl and HY zeolite was ground in a mortar before being heated at 350 °C for 15 h in flowing nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The as prepared catalyst was characterized using powder XRD, XPS, SEM with EDX, elemental mapping and HRTEM analysis. In the XRD spectra (Fig. 1), the Cu^I-Y zeolite shows identical pattern with HY zeolite, which proves that the incorporation of copper into the zeolite did not affect the overall structure of the Y zeolite. No observable peaks for CuCl solid indicates that there was no accumulation of CuCl solid in the Cu^I-Y zeolite, which suggests that Cu(I) was evenly distributed in the material. Notably, there was a significant decrease in the intensity of lower angle planes such as (111), (220) and (311) diffraction lines at 6.4, 10.4 and 12.1°, respectively, which indicates that the copper ions were exchanged into the framework structure. It has been reported that derived empirically relationship between the relative peak intensities of (220) and (311) reflections, I_{220} and I_{311}, in the XRD pattern is the indication of the replacement of Cu ions in the supercage of faujasite type zeolites.[38] As shown in Fig. 1, I_{220} was lower than I_{311} in Cu^I-Y, compared to the HY zeolite, which is the evidence for the exchange of Cu atoms in the supercage. From the SEM images (Fig. 2, a and b), it was observed that there was no significant change in the morphologies of the zeolites after the replacement of Cu(I) inside its cages. The HRTEM images showed that the Cu(I)-incorporated zeolites are spherical in nature with the size within range of 7-15 nm (Fig. 2, c and d). The elemental mappings of Si, Al, O and Cu are shown in Fig. 3. A pattern of dense-shallow distribution is obvious, which ought to be intrinsically associated with the internal structure of the molecular sieves.

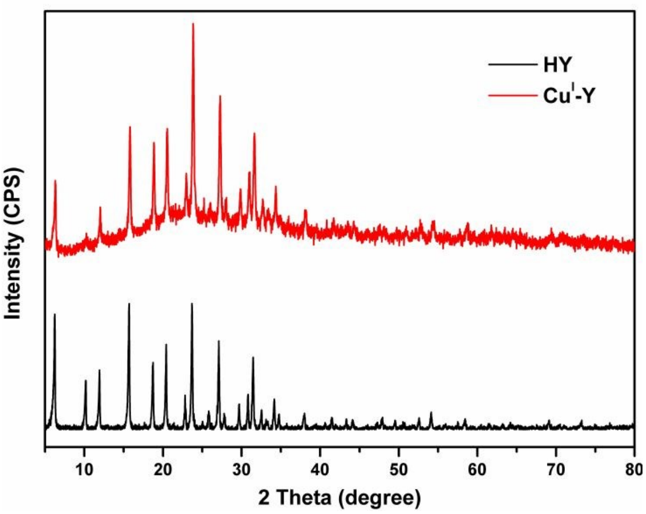

Fig. 1 The powder XRD patterns of HY and Cu^I-Y zeolites.

Elemental analysis from EDX results revealed about 22 wt. % of copper in the framework of zeolite (Table S1). It was reported that CuCl promoted dealumination during the exchange.[42] But the final ratio of Si/Al was found to be 2.6 which indicates that there was no loss of Al during the high temperature vapour phase exchange. Consequently, the total Cu/Al ratio was found to be 1:1. These observed results are in good agreement with what was reported by other authors.[39]

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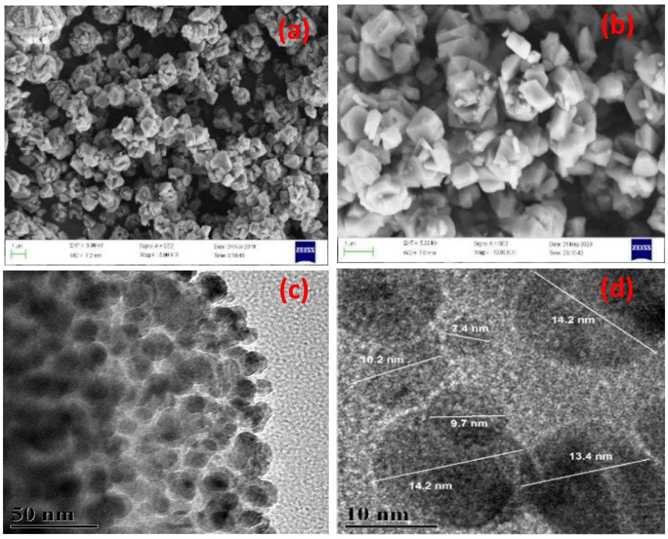

Fig. 2 SEM images of HY (a), Cu^I-Y (b), HRTEM images of Cu^I-Y (c) and (d).

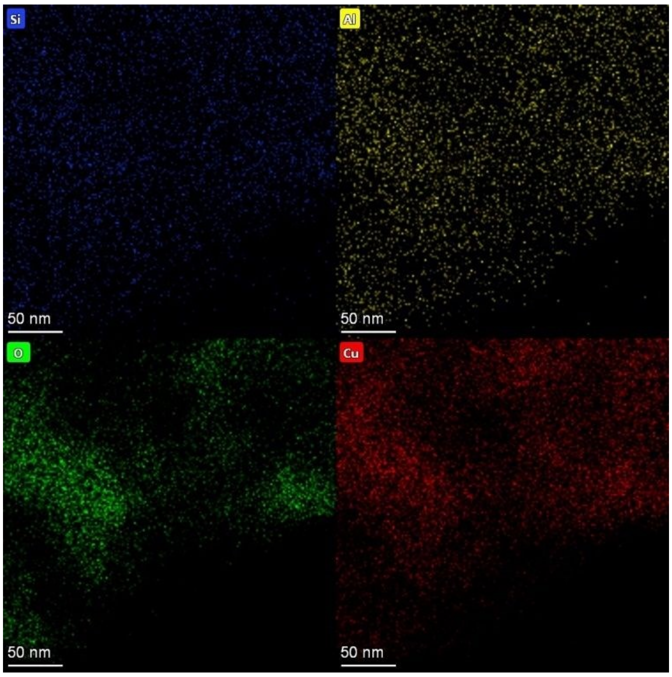

Fig. 3 Elemental mapping images of Si, Al, O and Cu in Cu^I-Y zeolite catalyst.

To investigate the chemical composition and electronic states of elements in the as prepared Cu^I-Y zeolite, XPS analyses were conducted (Fig. 4). The characteristic peaks for Al2p was found at 74.78 and 77.68 eV, respectively, which confirmed the presence of Al_2O_3 species (Fig. 4a).[34] The major peak observed at 101.98 eV was assigned to the Si2p of Si_2O_3. The other two deconvoluted peaks at 102.58 and 103.18 eV were assigned to SiO_2 (Fig. 4b). At O1s core level, a broad range of deconvoluted peaks were observed at 530.80, 531.70 and 532.50 eV which were assigned to the oxygen atom from O-Cu^+ bond, Si-O-Al linkage and Si-O-Si linkages, respectively (Fig. 4c). At Cu2p core level, the binding energies for $Cu2p_{3/2}$ and $Cu2p_{1/2}$ of cuprous ion were found at 932.25 eV and 952.13 eV, respectively. Because Cu^+ is vulnerable to O_2, it is not surprising to find weak signals for cupric ions ($Cu2p_{3/2}$) at 934.46 and 954.50 eV and a satellite peak located at 943.18 eV, the essential characteristics of Cu^{2+} (Fig. 4d). These observations indicate clearly that the copper present in the catalyst is predominantly in oxidation state +1.

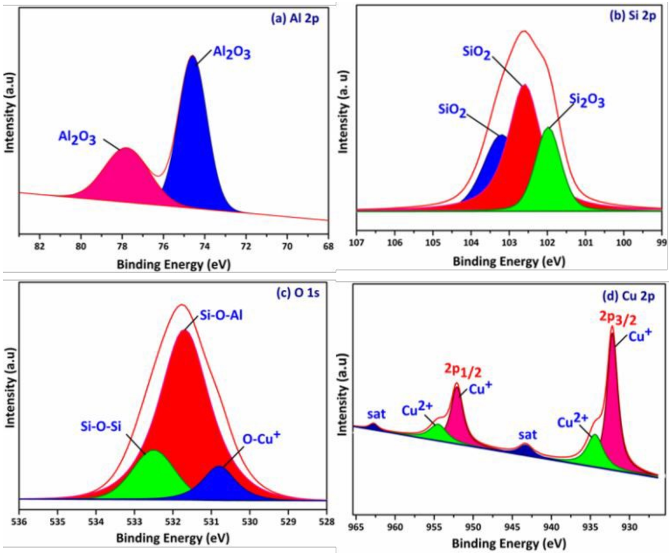

Fig. 4 XPS spectra of fresh Cu^I-Y zeolite catalyst: (a) Al2p; (b) Si2p; (c) O1s and (d) Cu2p, respectively.

2.2 Catalytic activity of Cu^I-Y zeolite on aerobic oxidation of benzyl alcohol

For comparison, various zeolites were employed as catalysts to catalyse the oxidation of benzyl alcohol using air as the oxidant. The obtained results were presented in Table 1. Blank experiments without the zeolite catalyst resulted in no oxidation (Table 1, entries 1 and 2). The original zeolite HY, the Bronsted acidic type, did not show any activity in the oxidation of benzyl alcohol under the same conditions (Table 1, entries 3 and 4). The combination of Cu^{II}-Y with TEMPO gave low yield in the aerobic oxidation of benzyl alcohol to benzaldehyde. Addition of a base or ligand along with TEMPO, the catalytic activity of the Cu^{II}-Y improved slightly (Table 1, entries 5-9). This is in opposite to what was observed for the Cu^I-Y zeolite. Cu^I-Y zeolite exhibited the best activity in combination with TEMPO, and NMI and other bases deteriorated the reaction (Table 1, entries 11-15). This is interesting that in the case of Cu_2O system, external ligand such as NMI is essential to ensure its effectiveness in similar aerobic oxidation.[47] The main reason for this is that the active sites of copper might be blocked by the coordination of ligands such as NMI and Cl^- which inhibited the oxidation *via* probably blocking the access of the substrate to the catalytic site. This effect would be particularly significant in the pores of the zeolite catalyst.

Table 1 The activities of various zeolites on catalysing aerobic oxidation of benzyl alcohol in acetonitrile with or without a base / TEMPO.[a]

Entry	Catalyst	Base	TEMPO (mg)	[b] Yield (%)
1.	-	NMI	-	-
2.	-	NMI	39	Trace
3.	HY	-	39	-

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4.	HY	NMI	39	-
5.	Cu^{II}-Y	-	39	9
6.	Cu^{II}-Y	NaCl	39	33
7.	Cu^{II}-Y	NMI	39	57
8.	Cu^{II}-Y	NaOH	39	31
9.	Cu^{II}-Y	K_2CO_3	39	48
10.	Cu^{I}-Y	-	-	Trace
11.	Cu^{I}-Y	-	39	61
12.	Cu^{I}-Y	NaOH	-	Trace
13.	Cu^{I}-Y	K_2CO_3	39	13
14.	Cu^{I}-Y	NaCl	39	3
15.	Cu^{I}-Y	NMI	39	16

[a] Reaction conditions: Benzyl alcohol (1 mmol), zeolite catalyst (100 mg), TEMPO (39 mg, 0.25 mmol which 25% based on the substrate), base (0.25 mmol), solvent (3 mL), 24 hrs, room temperature under atmospheric air.

[b] Determined by GC analysis using 1,2-dichlorobenzene as internal standard.

Like other copper-based catalyst, a radical co-catalyst is essential to drive the aerobic oxidation. In this work, TEMPO was employed by considering its low cost. Increasing the quantity of TEMPO in the reaction improved steadily the reaction yield (Table 2, entries 11-13). It seems that the activity of copper-based catalysts varies very much with solvents. Previously, we reported that acetonitrile was the most effective solvent in homogeneous system, CuI-NMI-TEMPO.[15] However, among the solvents examined, ethanol was the best solvent (Table 2, entry 10) for the zeolite catalyst. As the solvent, ethanol does not undergo oxidation of the same kind due to that the system is not strong enough to oxidise aliphatic alcohols. Raising temperature significantly reduced the usage of TEMPO without compromising the reaction yield and selectivity (Table 2, entries 14-16). Notably, under N_2 atmosphere, the reaction yield varies with the amount of TEMPO (Table 2, entries 17-19). These results suggest that the TEMPO acts only as an oxidant when O_2 is absent. These yields are close to the stoichiometrically expected ones, 12.5, 25 and 50%, when 0.25, 0.50 and 1.0 mmol of TEMPO was used, respectively. It also implies that in the catalysis, the formed TEMPOH is oxidised back to TEMPO by oxygen. When the reaction was exposed to atmospheric air, the yield raised quantitatively under the same conditions (Table 2, entry 16) in which the air is the oxidant and the TEMPO as co-catalyst. Throughout the investigation, the reaction temperature was set as 60 °C. The effect of catalyst loading was further studied with a range of amount from 25 to 125 mg of the catalyst. Unsurprisingly, the overall rate was found to increase with the amount of catalyst employed in the reaction, Fig. 5. It was found that quantitative and selective conversion of the substrate into benzaldehyde (over 99%) could be ensured under following optimal conditions, Cu^{I}-Y zeolite (100 mg, *ca*. 22 mg of Cu, 0.34 mmol), TEMPO (39 mg, 0.25 mmol), 18 hours, 60 °C under atmospheric air.

Table 2 The effect of solvent and the quantity of TEMPO on the aerobic oxidation of benzyl alcohol.[a]

Entry	Solvent (mL)	TEMPO (mg / mmol)	[b] Yield (%)
1	CH_3CN	39 / 0.25	61
2	THF	39 / 0.25	56
3	CH_2Cl_2	39 / 0.25	31
4	CH_3Cl	39 / 0.25	30
5	H_2O	39 / 0.25	19
6	DMF	39 / 0.25	21
7	DMSO	39 / 0.25	19
8	Toluene	39 / 0.25	13
9	CH_3CN/H_2O	39 / 0.25	31
10	C_2H_5OH	39 / 0.25	69
11	C_2H_5OH	50 / 0.32	78
12	C_2H_5OH	65 / 0.42	89
13	C_2H_5OH	75 / 0.48	99
[c]14	C_2H_5OH	39 / 0.25	73
[d]15	C_2H_5OH	39 / 0.25	83
[e]16	C_2H_5OH	39 / 0.25	>99
[f]17	C_2H_5OH	39 / 0.25	13
[f]18	C_2H_5OH	78 / 0.50	30
[f]19	C_2H_5OH	156 / 1.0	43

[a] Reaction conditions: Benzyl alcohol (1 mmol), Cu^{I}-Y zeolite (100 mg), TEMPO (39 mg), solvent (3 mL), room temperature, 24 hrs under atmospheric air.

[b] Determined by GC analysis using 1,2-dichlorobenzene as internal standard.

[c] 40 °C in 24 hrs under air

[d] 50 °C in 24 hrs under air

[e] 60 °C in 18 hrs under air

[f] 60 °C in 18 hrs under N_2 atmosphere.

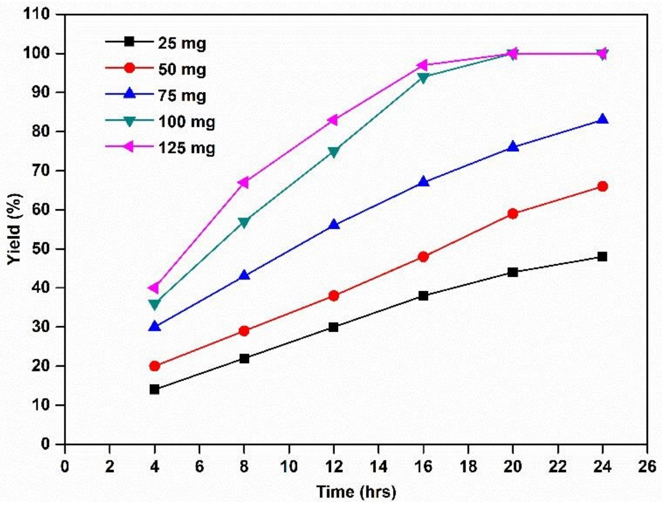

Fig. 5 Effect of catalyst loading for the aerobic oxidation of alcohol (Benzyl alcohol, 1 mmol; TEMPO, 39 mg; EtOH, 3 mL; 60 °C, air).

2.3 Heterogeneity and Reusability of the catalyst

To check the heterogeneity of the catalyst, a set of normal reactions under optimized conditions were performed and the progress of the reactions were monitored for every 2 hours. At 10 hours, the catalyst was removed from one of the parallel experiments to allow the reaction to continue under the same conditions and no further conversion was observed with the removal of the catalyst (Fig. 6, black) despite the presence of trace amount of bleached copper in the solution (<2% estimated by ICP-MS analysis). In other words, the bleached copper species did not catalyse substantially the reaction homogeneously. These findings suggested clearly that the oxidation was catalysed by the heterogeneous catalyst.

The reusability of the catalyst was also examined for the selective oxidation of benzyl alcohol under the optimized reaction conditions through repetitive runs. After the completion of the reaction, the catalyst was filtered and washed at least four times first with ethyl acetate and then water. The recovered catalyst was dried and reactivated at 350 °C for 4 h under N_2 atmosphere. Fig. 7 shows the reusability of the Cu^{I}-Y zeolite catalyst. In the first three runs, the activity of the catalyst kept essentially unchanged and more significant deterioration was observed afterwards. The decrease in activity might come from the formation of CuO caused by the oxidation of the Cu^{I}-Y catalyst since p-XRD and XPS results suggested significant increase in content of CuO in the recycled catalyst. As shown in Fig. 8, two new diffraction peaks were observed at 35.69 ° and 38.84 ° which belong to the planes (11-1) and (111) of CuO, respectively.

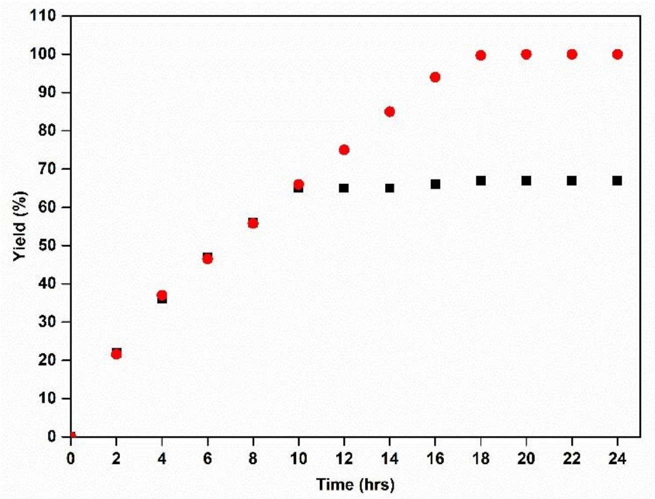

Fig. 6 Heterogeneity of the Cu^{I}-Y zeolite catalyst in the aerobic oxidation of benzyl alcohol under the optimal reaction conditions (Black square: the catalyst was removed when the reaction proceeded to 10 hrs and red circle: the reaction was kept undisturbed under the same conditions).

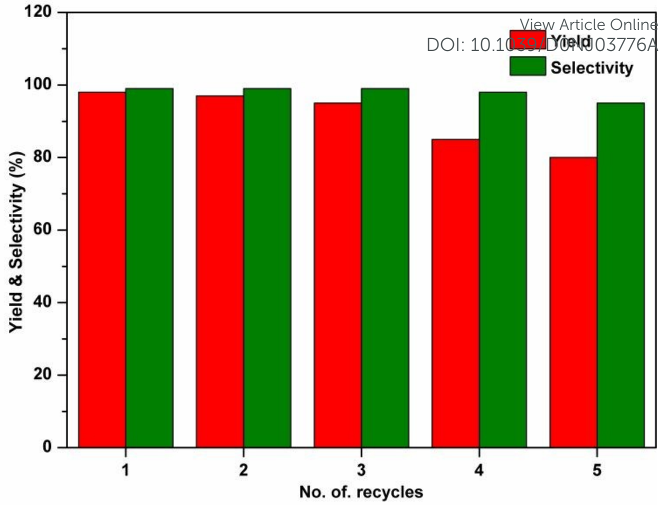

Fig. 7 Reusability of Cu^{I}-Y zeolite for the aerobic oxidation of benzyl alcohol.

The XPS spectra of recycled catalyst (5th recycle) was showed in Fig. 9. Compared to the spectra of the as prepared catalyst (Fig. 4), there were no obvious difference in both intensity ratio of related peaks and binding energies of the framework atoms (Al and Si) in the recycled catalyst, which suggested that the overall framework of the zeolite did not change and possessed excellent thermostability.

However, substantial differences were observed in the O1s and Cu2p spectra of the recycled catalyst. In the O1s core level, there was a slight decrease in relative peak area of the O-Cu^+ bond at 530.90 eV which implies the loss of copper(I) due to bleaching. It was also evident from the Cu2p core level spectrum with decrease in peak area of Cu^+ ion and the binding energies of $Cu2p_{3/2}$ and $Cu2p_{1/2}$ shifted to 932.28 eV and 952.00 eV, respectively. Since the chemical bleaching (*ca*. 2% for each run) is neglectable, the decrease in Cu^+ signals was mainly attributed to its conversion into Cu^{2+} as suggested by the significant increase in the peak area of the Cu^{2+} peaks found at 934.88 and 954.98 eV and two new shoulder peaks at 941.38 and 943.18 eV which originated from $Cu2p_{3/2}$. These changes confirmed the formation of CuO in the recycled catalyst which led to the decrease in the reaction yield.

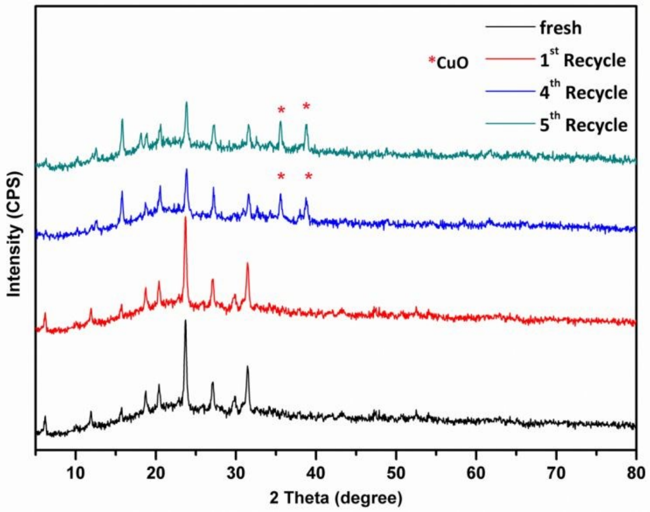

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Fig. 8 The comparison of p-XRD results of fresh and reused Cu^{I}-Y zeolites.

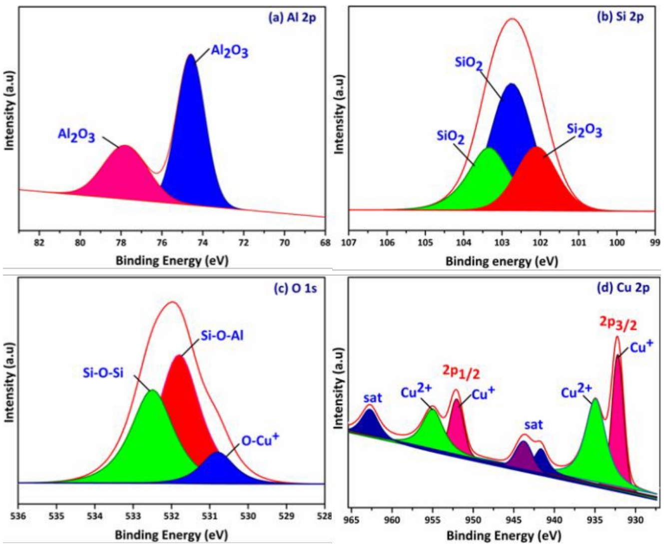
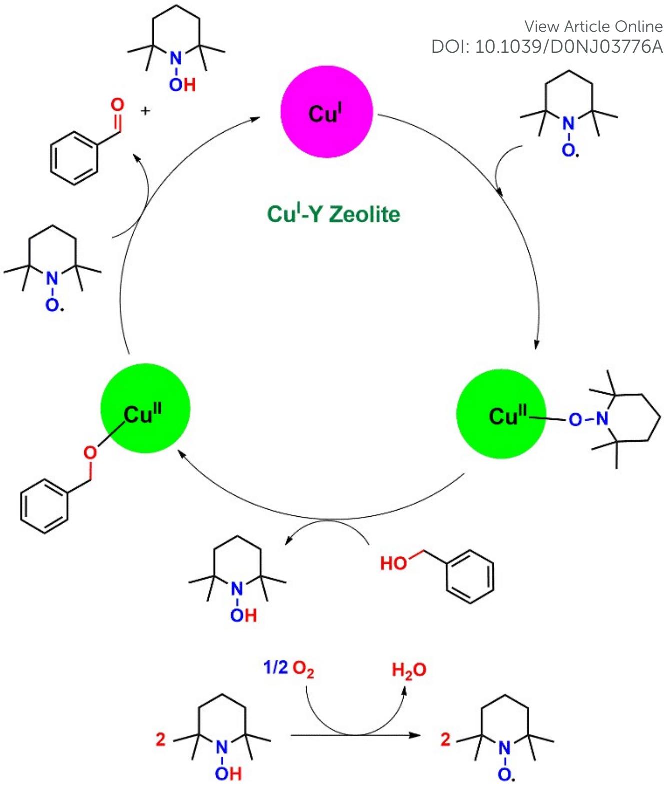


Fig. 9 XPS spectra of reused Cu^{I}-Y zeolite (5th recycle): (a) Al2p; (b) Si2p; (c) O1s and (d) Cu2p respectively.

2.4 Possible mechanism for the aerobic oxidation of benzylic alcohols catalysed by Cu^{I}-Y zeolite

There have been intensive investigations into the catalytic mechanism for Cu(I)-based catalysts for homogenous catalysis.[14] Based on this homogenous catalytic mechanism, a simplified mechanism for the aerobic oxidation of benzylic alcohols catalysed by Cu^{I}-Y zeolite was analogously proposed, Scheme 1. In the mechanism, it starts with the oxidative oxidation of Cu(I) to Cu (II) by TEMPO. Although the reduction potential for TEMPO is rather negative (*ca*. -2 V *vs*. Fc^{+}/Fc), the reduction would be much easier when it is coupled to proton to form TEMPOH, promoted by the proton coupled electron transfer (PCET) process.[48-51] The formed Cu(II) site is then ready to bind the substrate to accompanying the cleavage of TEMPOH. Although these processes are described in two separate steps in Scheme 1, practically, they proceed concertedly. The formed Cu^{II}-alkoxide undergoes H-atom abstraction mediated by TEMPO and further one electron transfer from the formed substrate radical to the metal to finalise the oxidation and bring the copper back to Cu(I). The formed TEMPOH in the catalysis would be oxidised back to its oxidised form, TEMPO, by the atmospheric oxygen. This is supported by the catalysis performed without the involvement of air, which gave only a yield roughly the same as the stoichiometric yield calculated based on the quantity of the added TEMPO.



Scheme 1 Plausible mechanism for the aerobic oxidation of benzylic alcohols catalysed by Cu^{I}-Y zeolite co-catalysed by TEMPO.

2.5 Substrate scope and comparison with other reported catalytic systems

To explore the versatility of the present catalytic system, various alcoholic substrates were employed under the optimized reaction conditions and the results are summarized in Table 3. Benzylic alcohols bearing electron donating groups (EDGs) such as methoxy and methyl groups afforded quantitatively the desired aldehydes with excellent selectivity (≥99%) (Table 3, entries 1-5). In general, electron withdrawing groups (EWGs) did not show much influence on the reactions yields unless the EWG is extremely strong such as -CF$_3$ (Table 3, entry 15). Compared to the electronic influence from the substituents on the catalysis, steric effect seems to be more significant (Table 3, entries 5-7). Such an effect is more significant on the *ortho*-position than on the other two positions (*meta*- and *para*). It seems that EWG could somehow offset this steric effect (Table 3, entry 10). The catalytic system showed no harm on other functional group such as C=C double bond in the substrate, cinnamyl alcohol (Table 3, entry 16). The catalytic system showed low activity towards heterocyclic alcohols which is attributed to its coordination capability of the heterocyclic atoms (N, S) (Table 3, entries 17 and 18). Furthermore, the catalyst was not so efficient towards the oxidation of aliphatic primary alcohols and secondary alcohols (Table 3, entries 19-23). Compared to other reported heterogeneous copper catalysts, the present catalytic system could operate under mild conditions, Table 4. Overall, less reaction time, lower reaction temperature and no extra additives are needed. The employment of ethanol as the reaction solvent is another advantage, non-toxic and easy for recycling.

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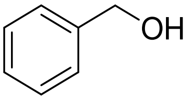
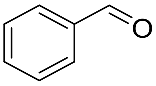
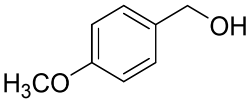
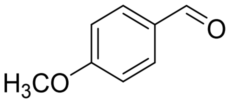
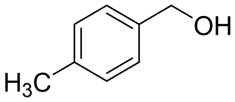
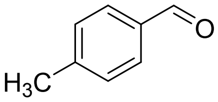
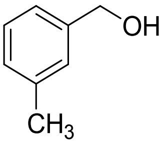
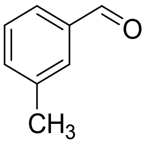
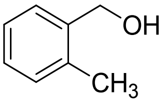
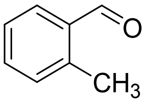
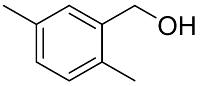
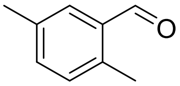
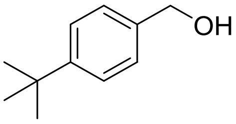
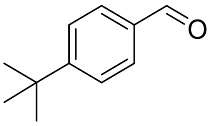
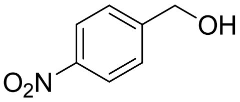
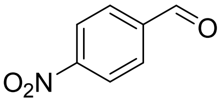
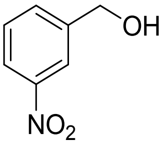
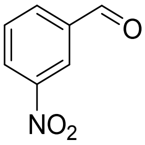
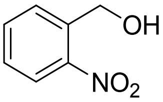
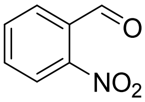
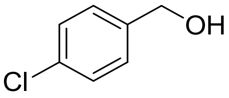
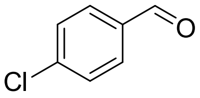
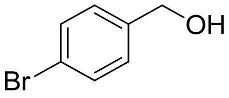
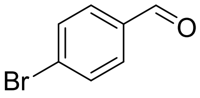
Table 3 Aerobic oxidation of various substrates catalysed by Cu^{I}-Y zeolite / TEMPO.[a]

Entry	Substrate	Product	Selectivity (%)	[b] Yield (%)
1.			>99	>99
2.			>99	>99
3.			>99	>99
4.			>99	99
5.			>99	91
6.			99	65
7.			99	80
8.			>99	>99
9.			>99	>99
10.			>99	>99
11.			>99	98
12.			99	98

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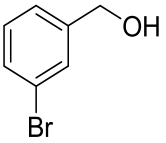
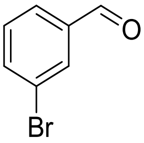
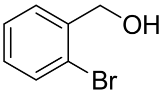
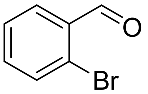
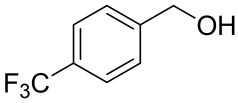
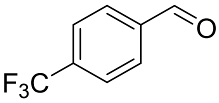
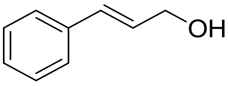
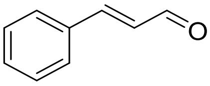
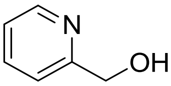
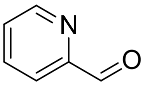
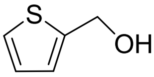
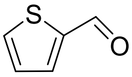
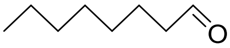
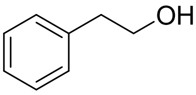
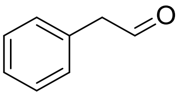
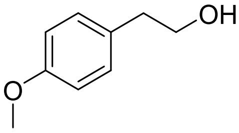
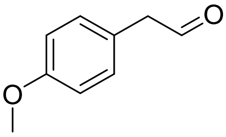
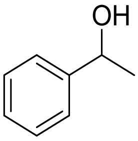
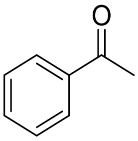
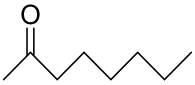
13.			98	89
14.			98	94
15.			>99	71
16.			98	87
17.			99	24
18.			99	53
19.			99	11
20.			99	6
21.			99	3
22.			99	1
23.			99	2

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[a] Reaction conditions: alcohol (1 mmol), Cu^I-Y zeolite (100 mg), TEMPO (39 mg), ethanol (3 mL), 60 °C, 18 h, atmospheric air.

[b] Selectivity and yield were confirmed by GC-MS analysis.

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Table 4 Comparison of this work with those reported in the literatures.

Entry	Reaction conditions	Solvent	Selectivity (%)	Yield (%)	Reusability	Ref.
1	**Cu^I-Y zeolite (100 mg), TEMPO, air, 60 ˚C, 18 h**	**Ethanol**	**>99**	**99**	**5 runs**	**This work**
2	RuO_2-Y zeolite (100 mg), air, 80 ˚C, 1.5 h	Toluene	>99	99	5 runs	46
3	Pd-NaX zeolite (100 mg), O_2, 100 ˚C, 4 h	Solvent- free	100	97	5 runs	45
4	SPS-Cu(II)@$Cu_3(BTC)_2$ (50 mg) , TEMPO, O_2, 75 ˚C, 8 h	MeCN	>99	99	10 runs	29
5	Cu-MnO_x (20 mg), O_2, 100 ˚C, 4 h	Toluene	98	98	-	28
6	Cu(I/II)-Amp-CPG (30 mg), TEMPO, O_2, 50 ˚C, 5.5 h	Solvent- free	99	97	7 runs	30
7	Cu@Tannin-OMP (20 mg), O_2, 1 MPa, 150 ˚C, 24 h	MeCN	>99	99	5 runs	17
8	CuO-rectorite (31 mg), TEMPO, K_2CO_3, O_2, 100 ˚C, 24 h	Toluene	>99	85	5 runs	19
9	$Cu_3(BTC)_2$ (150 mg), TEMPO, Na_2CO_3, O_2, 75 ˚C, 22 h	MeCN	98	89	2 runs	22
10	$(NH_4)_4[CuMo_6O_{18}(OH)_6]$ (11 mg), NaCl, O_2, 60 ˚C, 15 h	MeCN / H_2O	99	99	6 runs	21

3. Conclusions

In summary, an approach under mild conditions for aerobic oxidation of benzylic alcohols using Cu^I-Y zeolite as the catalyst has been developed. With TEMPO as the radical co-catalyst, air as the oxidant and ethanol as the solvent, a wide range of alcohols of the benzylic type could be quantitatively and selectively oxidised into corresponding aldehydes at 60 °C within 18 hours. In general, the catalytic system showed excellent tolerance in the substituents on the phenyl ring. Either EDGs or EWGs has little influence on the catalysis with one exception that strong EWG such as -CF_3 would considerably reduce the efficiency. Compared to the electronic nature, steric factor played more important role and the substituents at the *ortho*-position exerted more profound steric effect on the catalysis than *meta*- and *para*-positions. Such *ortho*- steric effect was observed in our recent report in which Cu_2O was the catalyst assisted with both TEMPO and N-methylimidazole (NMI).[47] But the effect was not as significant as what was observed in this work. This suggests the characteristic of the reaction occurring within the pores of the zeolite, which is certainly sensitive to the bulkiness of the substrates due to the space confinement within the pores. The catalyst is robust and reusable *via* simple filtration. The operation in ethanol is another advantage, which is environmentally benign and would be possible to recycle in industrial scale. The employment of the coinage metal copper and mild temperature of operation render the aerobic oxidation low cost and energy efficiency.

4. Experimental

4.1 Materials and Instrumentation

All reactions were carried out under open air atmosphere, with dry, freshly distilled solvents. All the chemicals were purchased from Aldrich, Macklin or Aladdin and used as received without further purification. The as-prepared Cu^I-Y zeolite was characterized by different spectroscopic methods. Powder X-ray diffraction (PXRD) measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (5-80 °) with scanning speed of 2 °/min. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the as prepared catalyst was measured by EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM. High resolution transmission electron microscopy (HRTEM) images were recorded using a Philips EM208 microscope operating at an accelerating voltage of 90 kV. XPS analysis was performed with an Al KR monochromator X-ray source operating at 15 kV using Thermo Fisher Scientific, USA. During spectrum acquisition, the test chamber pressure is maintained above 10^{-6} mbar for using low-energy electrons to expel electron guns to neutralize possible surface roughness. The progress of the catalytic reaction was monitored and quantitatively analyzed by gas chromatography (Agilent 7890) with a packed column of Restek capillary SE-54. The oxidised products were isolated and characterized by ^{1}H and ^{13}C NMR spectra recorded on Bruker NMR (400 MHz) instrument in $CDCl_3$.

4.2 Procedures for the preparation of NH_4^+-Y, Cu^{II}-Y and Cu^{I}-Y zeolites

NH_4^+-Y zeolite was prepared by mixing an aqueous solution of NH_4Cl (100 mL, 10%) into the suspension of NaY zeolite (5 g) in 100 mL deionised water and kept for stirring at 70 °C for 12 hours for ion exchange. The exchange was repeated at least three times. For each time, the zeolite powder was washed repeatedly with distilled water and then dried. All the cation- exchanged zeolites were activated at 450 °C for 3 h prior to use. Cu^{II}-Y zeolite was prepared in the same manner by using aqueous solution of $Cu(NO_3)_2 \bullet 3H_2O$ (100 mL, 10%). Cu^{I}-Y zeolite was prepared according to the procedure reported by Li *et al.*[42] NH_4Y zeolite was first loaded in a furnace and heated at 550 °C for 4 h to obtained HY zeolite. A mixture of CuCl (350 mg, 3.53 mmol) and HY (1 g) were ground in a mortar and then heated in a furnace under flowing nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The ion-exchange of Cu(I) in solid CuCl with H^+ in HY zeolite occurred at over 300 °C and the maximum ion-exchange rate was reached at 340 °C with the consequent release of HCl gas. Cu^{I}-Y was prepared at two different temperatures *via* heating the mixture of CuCl/HY at 350 °C for 15 h or 450 °C for 6 h under nitrogen atmosphere. After the preparation was over, the Cu^{I}-Y was kept in vacuum.

4.3 Aerobic Oxidation of alcohols using Cu^{I}-Y zeolite

100 mg of freshly prepared Cu^{I}-Y zeolite was taken in a reaction tube (15 mL) containing ethanol (3 mL) as a solvent. A mixture of benzyl alcohol (1 mmol) and TEMPO (0.25 mmol, 39 mg) were added simultaneously to the reaction tube and stirred at 60 °C for 18 h. The aliquots of the reaction mixture were used for product analysis at regular interval by gas chromatographic technique. The retention times for various compounds were determined by injecting pure compounds under identical GC conditions. The yield of benzaldehyde was calculated from GC analysis using 1,2-dichlorobenzene (0.1 mL) as the internal standard. For other substrates, the oxidation reaction was analogously performed. The yield of products was calculated from GC data and the oxidation products were identified from GC-MS results. For isolation of selected compounds, column chromatography was performed on silica gel 60-120 mesh with a mixture of petroleum ether and ethyl acetate (95:5) solvent as eluent. In repetitive run, the catalyst was separated by filtration, followed by solvent evaporation under reduced pressure. The recovered catalyst was thoroughly washed with ethyl acetate and water. Then it was dried and reactivated at 350 °C for 4 h under N_2 atmosphere before next run.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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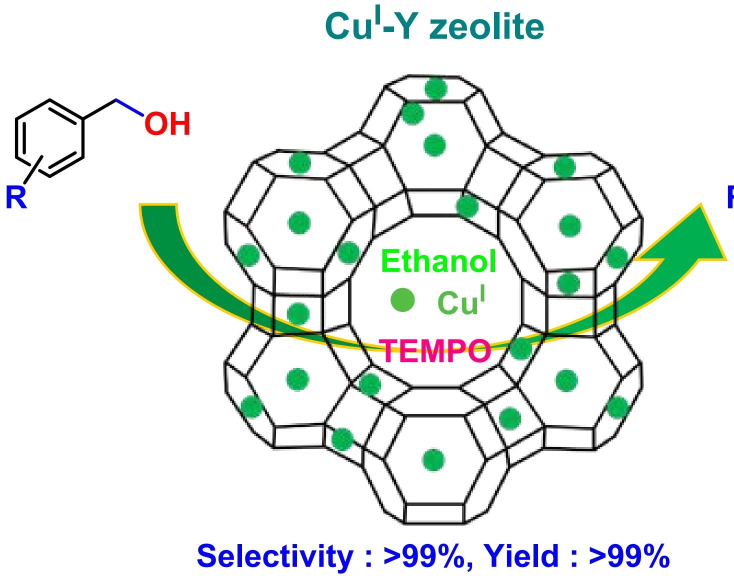

Cu^{I}-Y zeolite catalyst, which is robust and recyclable, assisted with TEMPO catalyses quantitatively the aerobic oxidation of a wide range of benzylic alcohols into aldehydes in ethanol under mild conditions without additional additives.