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Aerobic Oxidation of Alcohols Enabled by Nitrogen-Doped Copper Nanoparticle Catalysts

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Heterogeneous nitrogen-doped carbon-incarcerated copper nanoparticle catalysts have been developed. The catalysts promoted oxidation of alcohols to the corresponding aldehydes, including aliphatic substrates, in high yield in the presence of N-oxyl radical co-catalyst. The catalysts were applied to a flow reaction and a long lifetime (up to >5 days) was achieved by tuning the flow rate of oxygen gas. By applying the catalysts, two-step, sequential, continuous-flow synthesis of unsaturated carbonyl compounds was demonstrated, and the product was further converted into a bioactive heterocycle without isolation of intermediates.

Introduction

Heterogeneous catalysts have been actively studied in recent years because they are suitable for realizing environment-friendly reactions. Continuous-flow reaction systems using columns packed with heterogeneous catalysts are favourable in terms of efficiency and safety.[1,2] Furthermore, generated reactive intermediates can be converted immediately in sequential-flow systems through tandem-type reactions using connecting columns. Such systems make it possible to design a range of synthetic routes involving unstable intermediates.[3–5] However, synthetic organic reactions in flow systems that use heterogeneous catalysts are less developed, primarily because of the reduced activity and/or durability of catalysts.
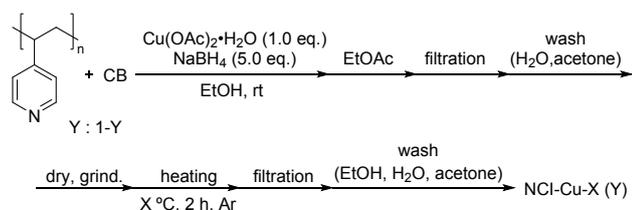
Aerobic oxidation of alcohols to aldehydes is a crucial organic reaction because starting materials are readily available and products can be utilized in a wide range of organic reactions. Catalytic systems with a Cu complex and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as an *N*-oxyl radical co-catalyst offer a convenient way to oxidize alcohols to aldehydes. Since the first report in 1984,[6] homogeneous catalyst systems have been further improved and applied to a wide variety of substrates, including aliphatic alcohols, which are generally more difficult to oxidize than are aromatic alcohols.[7–10] Immobilization of metal catalysts for these reactions is desirable considering that metals are toxic and may interrupt subsequent reactions when applied to tandem reactions. There are many reports of heterogeneous copper catalysts for these reactions; however, a tedious process to prepare catalysts is required, and in most cases, the application of these systems to aliphatic alcohols is limited.[11–25]

Metal nanoparticles (NPs) can form heterogeneous catalysts with promising potential because they tend to have good robustness and can be easily immobilized. Although several groups have reported heterogeneous Cu NP catalysts for the aerobic oxidation of alcohols with TEMPO,[26–29] harsh reaction conditions are generally necessary. More importantly, aliphatic alcohols are rarely applied in these reports. We hypothesized that further activation of Cu NPs by ligands would be necessary to construct highly active catalysts, considering that successful homogeneous catalyst systems utilized bipyridine ligands for copper.[7] We previously developed nitrogen-doped carbon-incarcerated metal NP catalysts (NCI-M) prepared from poly-4-vinylpyridine as a nitrogen source.[30,31] These catalysts showed high activity for several oxidation reactions that rarely occurred with metal NPs supported on nitrogen-free carbon black (CB). Despite the remarkable effects of nitrogen dopant, the combination of nitrogen-doped carbon-supported catalysts and other co-catalysts is less explored. Inspired by these results, herein, we report nitrogen-doped carbon-supported Cu NP catalysts for aerobic oxidation of alcohols to aldehydes, including aliphatic substrates, with high yield and reusability in both batch and flow systems.

Results and discussion

NCI-Cu catalysts were synthesized by following a method we developed (Scheme 1).[30] Poly(4-vinylpyridine) (P4VP) as a nitrogen source and CB were mixed in EtOH, and Cu NPs were then formed in situ by reduction of a metal source with NaBH4. After the addition of EtOAc to precipitate polymer-capsulated Cu NPs, the obtained solids were pyrolyzed at 300–900 °C to afford the solid catalysts, which were named NCI-Cu-X (Y), where X indicates the temperature of pyrolysis and Y is the weight ratio of P4VP in the starting material of supports. In this method, metal NPs were stabilized by multiple interactions from the nitrogen-containing polymer, and pyrolysis of the polymer-encapsulated metal NPs afforded well-dispersed and

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Scheme 1 Preparation of NCI-Cu catalysts

catalytically active species.

Several heterogeneous catalysts for the aerobic oxidation of alcohols to the corresponding aldehydes were examined in the presence of TEMPO and N-methylimidazole (NMI) (Table 1). Initially, we employed Cu NPs incarcerated in a composite of polystyrene-based co-polymer and CB (PI/CB-Cu) that we previously developed as highly robust heterogeneous catalysts[32]; however, only 7% of the desired aldehyde was observed (entry 1). The use of Cu NPs on SBA-15, a mesoporous silica that is widely used for support of heterogeneous catalysts, also gave a poor result (entry 2). On the other hand, NCI-Cu-800 (0.500) catalyzed the reaction in almost quantitative yield (entry 3). Furthermore, when the reaction temperature was reduced to ambient temperature, the yield remained around 90% (entry 4).

To achieve highly active catalysts for the oxidation of alcohols, aliphatic alcohol was then applied under these conditions and the catalyst preparation was optimized (Table 2). The yield dropped dramatically compared with the reaction with aromatic alcohols when either NCI-Cu-900 (0.500) or NCI-Cu-800 (0.500) was employed (entries 1 and 2). Control experiments showed that both copper and TEMPO were necessary for the oxidation reaction to proceed (Table S1 in Electronic Supplementary Material). As the pyrolysis temperature used for the preparation of the catalyst was decreased to 500 °C, the aldehyde yield increased to 38% (entries 3 and 4). NCI-Cu-400 (0.500) gave similar results to those with NCI-Cu-500 (0.500) (entry 5), but pyrolysis at 300 °C was not sufficient to activate the catalysts (entry 6). Increasing the amount of catalyst and TEMPO improved the result (entry 8). Based on these conditions, the ratio between CB and P4VP was studied (entries 7–12). Although excess amounts of P4VP (Y = 0.625) led to reduced yield of aldehyde, a ratio of Y = 0.500 gave a moderate yield (entries 7 and 8). It is probably because that too much nitrogen dopants would cap the active sites. Furthermore, the use of a small excess of CB such as the ratio Y = 0.325 or Y = 0.250 gave slightly better results (entries 9 and 10). However, a larger excess of CB (Y = 0.125) or catalysts without P4VP caused decreased yields (entries 11 and 12) indicating that nitrogen dopants activated copper species to accelerate the reaction. Scanning transmission electron microscope (STEM) analysis of NCI-Cu-500 (0.500) and Cu/C-500 showed that large aggregates (20-50 nm) were observed in both catalysts (Figures S3 and S4). In addition, larger ones (>100 nm) were observed for NCI-Cu-500 (0.500), indicating that the superior performance of NCI-Cu-500 cannot be explained by a simple size effect.

Table 1 Oxidation of aromatic alcohol with catalyst systems

Entry	Catalyst	Temp. /°C	Yield[a] /%
1	PI/CB-Cu	60	7
2	SBA-15-Cu	60	25
3	NCI-Cu-800 (0.500)	60	99
4	NCI-Cu-800 (0.500)	30	88

[a] Determined by GC analysis.

Table 2 Oxidation of aliphatic alcohol with NCI-Cu catalysts

Entry	NCI catalyst	Yield[a] /%
1	NCI-Cu-900 (0.500)	16
2	NCI-Cu-800 (0.500)	15
3	NCI-Cu-650 (0.500)	23
4	NCI-Cu-500 (0.500)	38
5	NCI-Cu-400 (0.500)	35
6	NCI-Cu-300 (0.500)	27
7[b]	NCI-Cu-500 (0.625)	37
8[b]	NCI-Cu-500 (0.500)	61
9[b]	NCI-Cu-500 (0.375)	67
10[b]	NCI-Cu-500 (0.250)	66
11[b]	NCI-Cu-500 (0.125)	58
12[b]	Cu/C-500[c]	41
13[d]	NCI-Cu-500 (0.375)	74
14[d]	NCI-Cu-400-5 h (0.375)[e]	81

[a] Determined by GC analysis. [b] Cu: 2.0 mol%, TEMPO: 15 mol%, NMI: 5.0 mol%. [c] The catalyst was prepared without using P4VP. [d] Cu: 2.0 mol%, TEMPO: 30 mol%, NMI: 5.0 mol%. [e] The catalyst was prepared by pyrolysis for 5 h.

The use of 30 mol% of TEMPO improved the yield to 74% (entry 13). Further optimization of the conditions of pyrolysis gave the best results when the catalyst was prepared by pyrolysis at 400 °C for 5 h (entry 14). With the best catalyst, we checked the metal leching by inductively coupled plasma (ICP) of the crude mixture. In the reaction with aliphatic alcohols, 3.4% of the copper used for the reaction leaching was observed, while in the reaction with aromatic alcohols, only 0.3% of the copper was leached out.

With the optimized conditions established, the substrate scope for the oxidation of alcohols was investigated (Scheme 2). Alkyl-substituted benzyl alcohols gave the desired products **2a** and **2b** in excellent yields. Benzyl alcohols with halogen **1c–e**, electron-donating **1f**, or electron-withdrawing groups **1i** and **1j** were converted into corresponding aldehydes smoothly. Substituents on the o- or m-position did not disturb the reaction (**2e**, **2g**, **2h**), and naphthyl **1k** and piperonyl alcohol **1l** were also suitable substrates for this reaction. Cinnamyl aldehyde **2m** and heteroaromatic aldehydes **2n** and **2o** were obtained in good to excellent yields. Aliphatic alcohols also gave the corresponding
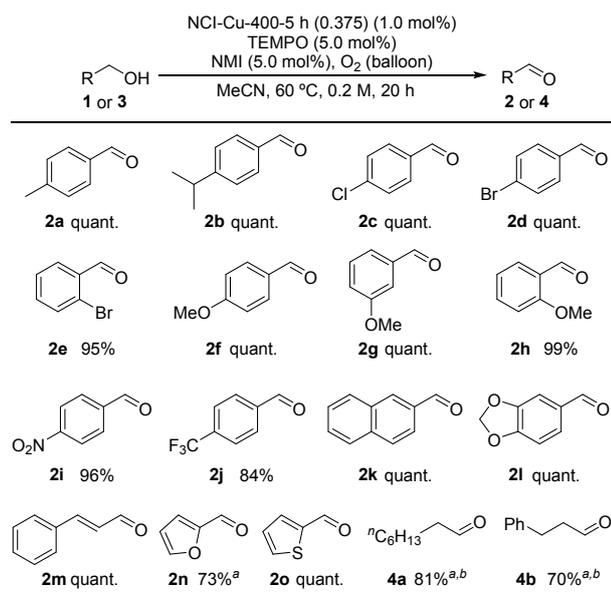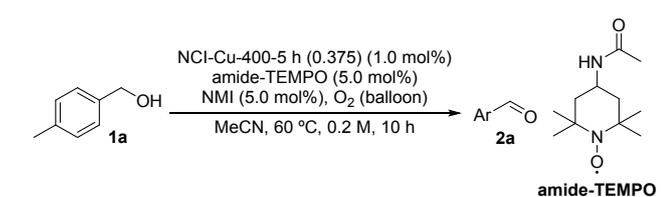
Scheme 2 Substrate scope. [a] Determined by GC analysis. [b] NCI-Cu (2.0 mol%), TEMPO (30 mol%).

Scheme 3 Oxidation reaction in continuous flow. MFC stands for mass flow controller.

aldehydes **4a** and **4b** selectively in good yields when the amounts of catalyst and TEMPO were increased. Various alcohols, including aliphatic alcohols, could be applied to these systems by using small amounts of Cu catalysts.
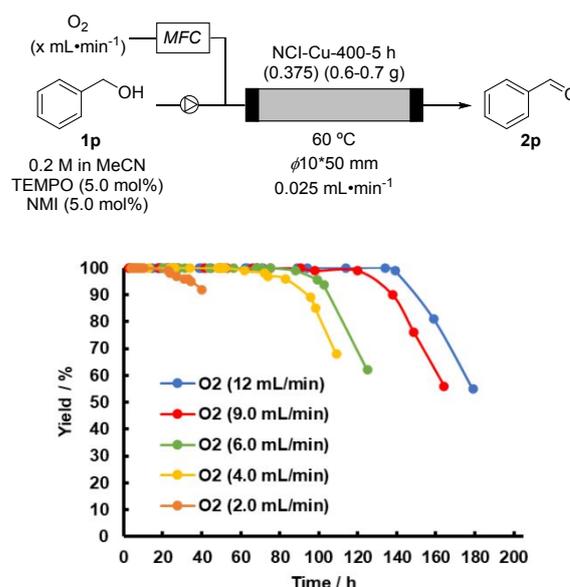
The catalysts were easily recovered by simple filtration and their reuse was examined (Table 3). However, the yield dropped to 85% from the second run in the presence of TEMPO under the optimized conditions (entries 1 and 2). We found that the use of 4-acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl (amide-TEMPO) instead of TEMPO led to excellent catalytic activity being maintained (entries 3–5). This improved activity may be due to the higher oxidation potential of this compound brought about by the electron-deficient substituent.[33] Moreover, quantitative yields were observed for at least five

Table 3 Recycling test with the catalysts

Entry	NCI-Cu catalysts	N-oxyl radical	Yield[a] /%
1	1st use	TEMPO	>99
2	2nd use	TEMPO	85
3	1st use	amide-TEMPO	99
4	2nd use	amide-TEMPO	99
5	3rd use	amide-TEMPO	80
6[b]	1st use	amide-TEMPO	>99
7[b]	2nd use	amide-TEMPO	>99
8[b]	3rd use	amide-TEMPO	>99
9[b]	4th use	amide-TEMPO	>99
10[b]	5th use	amide-TEMPO	>99

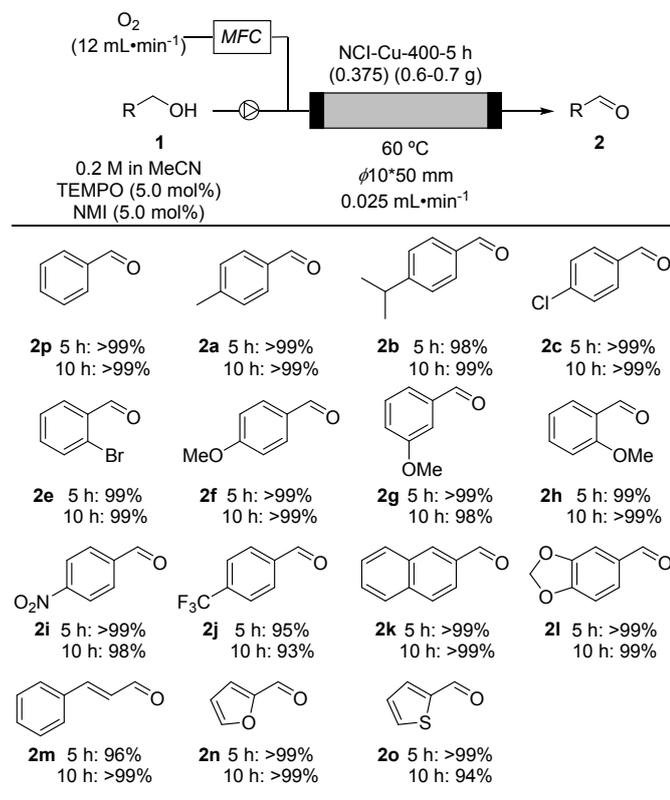[a] Determined by GC analysis. [b] Cu: 2.0 mol%.

runs with 2 mol% NCI-Cu catalyst (entries 6–10).

We investigated the oxidation systems in continuous flow by using a column packed with NCI-Cu catalysts (Scheme 3). A solution of benzylic alcohol **1p**, TEMPO, and NMI in acetonitrile was flowed into the column, and the flow rate of O_2 was controlled by a mass-flow controller. It was found that the lifetime depended on the flow rate of O_2. When the flow rate of O_2 was 2.0 mL/min, benzaldehyde **2p** could be obtained in 99% yield for 23 h, and the yield gradually decreased after 23 h. As the flow rate was increased to 4.0, 6.0, 9.0, or 12 mL/min, the lifetime of the catalyst whereby quantitative yield was maintained, was prolonged to 62, 88, 120, or 139 h, respectively. When the flow rate of O_2 was 12 mL/min, TON and TOF values were 393 and 2.9 h^{-1}, respectively, and space-time yield reached 194 g·L^{-1}·day^{-1}. Side-products such as carboxylic acids were not observed by either GC or ^{1}H NMR analysis.

Substrate scope was examined in flow under the optimal conditions (Scheme 4). The yields for all 15 substrates were excellent compared with batch systems, and no starting materials were observed at 5–10 h after the start of the reaction. The good reactivity in the flow system might be facilitated by the high mixing efficiency and the fast flow rate of O_2.

Encouraged by the results of flow reactions, a two-step, sequential continuous-flow system was designed to synthesize α,β-unsaturated ketones from alcohols via oxidation and aldol condensation. A solution of benzylic alcohol **1p**, TEMPO, and NMI in toluene was pumped at 0.075 mL/min into a column packed with NCI-Cu catalyst and reacted at 80 °C. The obtained crude solution was then degassed to remove oxygen and flowed with a solution of α-tetralone in toluene/iPrOH (4:1) into the next reactor packed with A-26 solid base catalyst, and then reacted at 60 °C (Scheme 5).[34] In the oxidation process, the solvent was changed from MeCN to toluene to avoid possible

reaction with the generated aldehydes in the condensation step.

Scheme 4 Substrate scope in flow systems. Yields were determined by GC analysis. MFC stands for mass flow controller.

Under these conditions, the desired unsaturated ketone **5** was obtained in 82%–90% yield for more than 50 h operation. We confirmed that no leaching of Cu was detected by ICP analysis of the fraction at the steady state (35 h after the reaction started). The crude product obtained from the sequential flow reaction could be converted into dihydropyrimidinone **6**, which is a candidate of pharmaceuticals,[35–39] in high yield by A-26 catalyzed condensation with thiourea in the batch system (Scheme 6).

To clarify the details of the surface composition and the effect of pyrolysis temperature, X-ray photoelectron spectroscopy (XPS) analysis was conducted (Figure 1). Two peaks were identified at 397.9–398.5 eV and 399.3–400.5 eV in the N 1s spectrum of both catalysts, which were assigned to pyrrolic nitrogen and pyridinic nitrogen, respectively.[40] In the case of NCI-Cu-800 (0.500), the pyrrolic moiety predominated (66%) compared with the pyridinic moiety. On the other hand, NCI-Cu-400-5 h (0.375) was composed of 56% pyridinic moiety for the *N*-doped carbon. Given that 2,2'-bipyridyl was the best
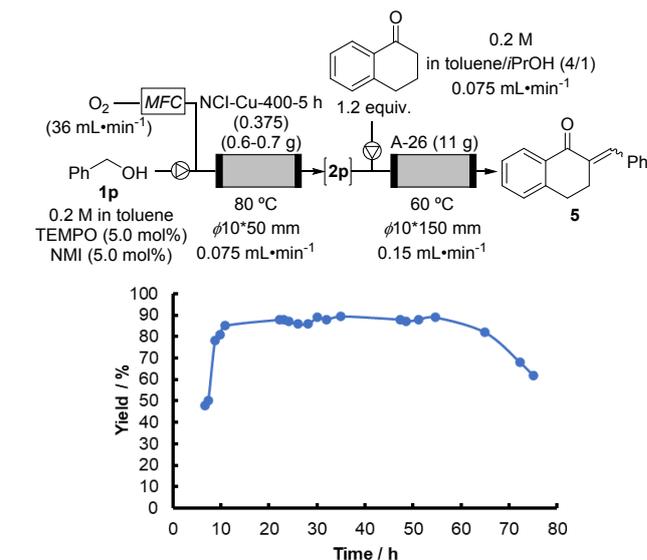
Scheme 5 Application to sequential- and continuous-flow systems. MFC stands for mass flow controller.
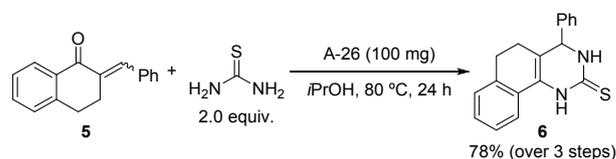
Scheme 6 Further conversion of ketone **5** into dihydropyrimidinone **6** in batch
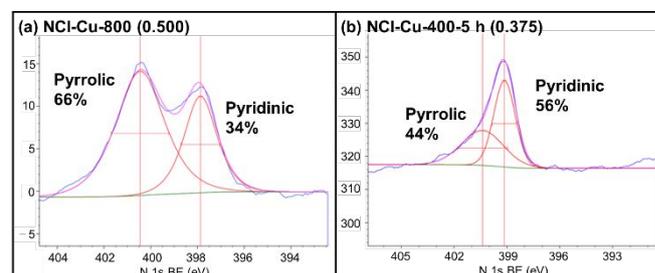

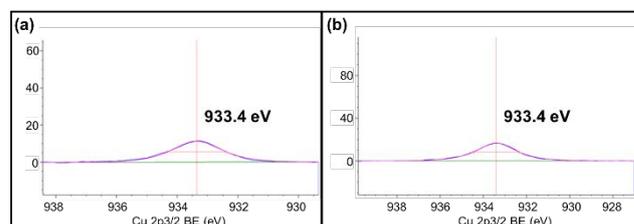**Figure 1** XPS analysis for nitrogen of the catalysts

Figure 2 XPS analysis for copper of the catalysts. (a) fresh NCI-Cu-400-5 h (0.375) (b) NCI-Cu-400-5 h (0.375) used in flow

ligand for alcohol oxidation in the homogeneous system developed by Stahl and co-workers,[7] the results indicate that the pyridinic moiety may act as a ligand to facilitate the reaction. Therefore, NCI-Cu-400-5 h (0.375), which has more abundant pyridinic nitrogen, gave much better results for the oxidation of alcohols.

We also attempted to analyze Cu species of the best catalyst before/after use in flow (Figures 2). In the Cu 2p3/2 spectrum of both cases, peaks were observed at 933.4 eV. Considering that the peak position does not change after the oxidation reaction, this peak can be assigned to CuO.[41] Therefore, catalyst deactivation through repeated use may not be caused by a change in the oxidation state of Cu species.

Kinetic studies under the continuous-flow conditions were conducted to clarify the cause of catalyst deactivation. We defined the moles hourly space velocity (MHSV) as:[42]

$$1/\text{MHSV (h)} = (\text{catalyst (mol)} \times \text{time (h)}) / \text{substrate (mol)}$$
$$= \text{catalyst (mol)} / (\text{concentration (mol/L)} \times \text{flow rate (L/h)})$$

MHSV is a molar ratio of the rate to supply a substrate to the catalyst amount in a unit of time. The kinetic constant (k) can be defined by the following equation when the reaction proceeds in first-order kinetics.

$$d[\text{alcohol}]/d[t] = -k[\text{alcohol}] \quad (t = 1/\text{MHSV})$$
$$\ln(\text{conversion}) = -k/\text{MHSV}$$

We measured kinetic constants with different flow rates of O_2 or air (Table 4). As the flow rate of O_2 was decreased, the value of the kinetic constant also decreased (entries 1–3). Accordingly, the importance of the number of equivalents of O_2 and/or the faster flow rate to maximize the physical mixing efficiency might be suggested. To examine this possibility further, the reaction was conducted with air with a fast flow rate of 12 mL/min (entry 4). These conditions gave the smallest kinetic constant, with a value that was similar to the result when O_2 was flowed at 2.0 mL/min. These observations confirm that the number of
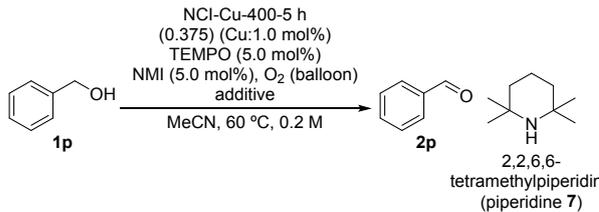
Table 4 Kinetic study with different flow rates of O_2 or air in flow
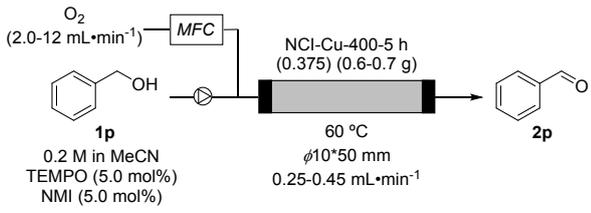
Entry	Gas flow	k
1	O_2 (12 mL/min)	17.9
2	O_2 (6.0 mL/min)	13.1
3	O_2 (2.0 mL/min)	6.23
4	Air (12 mL/min)	5.39

Determined by GC analysis. MFC stands for mass flow controller.

Table 5 Kinetic studies with additives in batch

Entry	Additive	k
1	NMI (1.0 equiv.)	0.972
2	-	0.205
3	H_2O (1.0 equiv.)	0.145
4	H_2O (100 equiv.)	0.112
5	piperidine **7** (1.0 equiv.)	0.0791

Determined by GC analysis.

equivalents of O_2 is more important for increasing the reaction rate for alcohol oxidation.

The effect of additives that could result in catalyst poisoning was investigated in batch systems (Table 5). We first speculated that NMI may accumulate in a catalyst column and block the active sites. Contrary to our expectation, when NMI was added, the highest reaction rate was measured (entry 1). Next, the effects of H_2O, which is generated during the reaction, were checked. It was found that higher amounts of water led to smaller kinetic constants compared with the optimal conditions (entries 2–4). We also examined 2,2,6,6-tetramethylpiperidine (piperidine **7**), which could be generated by the decomposition of TEMPO. In this case, the smallest k value was observed, indicating that accumulation of piperidine **7** may be a catalyst poison. Based on the results of kinetic studies and XPS analysis, deactivation of the catalyst might be caused by the accumulation of by-products/side-products such as H_2O and piperidine **7** in the column, rather than as a result of changes of the oxidation state of the Cu species. Since adsorption of byproducts can compete with adsorption of oxygen, high oxygen flow rates might contribute to prevent the deactivation.

Conclusions

NCI-Cu NP catalysts for oxidation of alcohols to aldehydes co-catalyzed by TEMPO were developed. A range of alcohols could be oxidized to aldehydes, including aliphatic alcohols, in good yields. These catalysts should be environmentally benign because the earth-abundant metal was immobilized, and could be reused at least five times. The catalysts were applicable to a flow reaction and their activity was maintained for more than 5 days. We found that the flow rate of oxygen gas affected the lifetime of catalysts, with higher flow rates leading to longer lifetime. This flow system was further applied for the rapid synthesis of dihydropyrimidinone, which was achieved by sequential oxidation/aldol condensation in continuous flow, followed by a solid-base-catalyzed condensation with thiourea in batch. Based on XPS analysis, the pyridinic moiety on the nitrogen-doped carbon might play a crucial role relative to the pyrrolic group. Kinetic studies suggested the possibility that

water and piperidine, which are generated by the decomposition of TEMPO, can act as a catalytic poison. These insights should be valuable for the development of aerobic oxidation reactions in continuous-flow systems with heterogeneous catalysts.

Data availability

Experimental procedures and compound characterization, are provided in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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