Controlled Aerobic Oxidation of Primary Benzylic Alcohols to Aldehydes Catalyzed by Polymer-Supported Triazine-Based Dendrimer–Copper Composites

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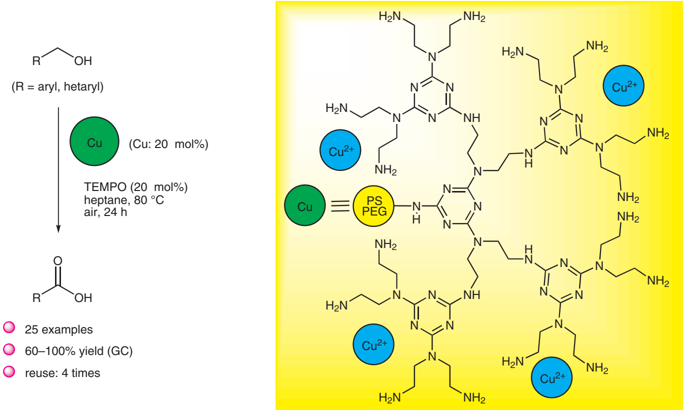

- 25 examples
- 60–100% yield (GC)
- reuse: 4 times

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Abstract A controlled aerobic oxidation of primary benzylic alcohols to the corresponding benzaldehydes by using polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported triazine-based polyethyleneamine dendrimer–copper complexes [PS–PEG-TD2–Cu(II)] was developed. In particular, PS–PEG-TD2–Cu(OAc)$_2$ efficiently catalyzed the aerobic oxidation of benzylic alcohols in the presence of a catalytic amount of TEMPO under atmospheric conditions to give the corresponding aldehydes in up to quantitative yield. The catalyst was readily recovered by simple filtration and reused four times without significant loss of its catalytic activity.

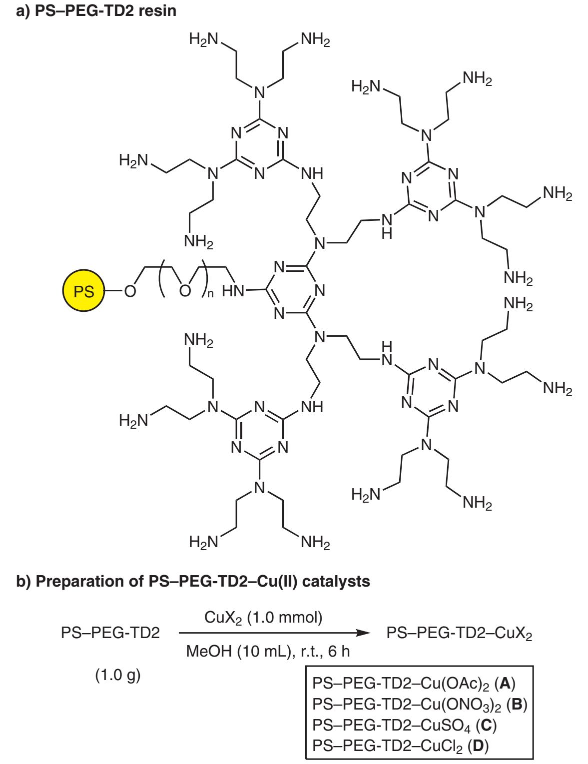
Key words dendrimer, aldehydes, aerobic oxidation, polymer support, copper catalysis

The controlled oxidation of primary alcohols to the corresponding aldehydes is an important and fundamental organic transformation.[1] Aerobic oxidation of alcohols has recently attracted much attention as a means of avoiding potential disposal issues, as no hazardous chemical waste from stoichiometric oxidants is formed as a co-product. On the other hand, heterogeneous catalysts have been recognized as powerful tools for realizing environmentally benign organic transformations because of the ease with which they can be recovered and reused.[2] Consequently, there are good reasons to believe that heterogeneous catalytic aerobic oxidation of alcohols might offer a more favorable green and clean alternative to conventional oxidation processes. Heterogeneous precious-metal catalysts such as Pd, Pt, or Ru are typically used in the aerobic oxidation of alcohols,[3] and therefore, further pursuit of green sustainable methods for aerobic oxidation of alcohols provides the challenge of replacing these scarce precious metals with more abundant ubiquitous metals.[4]

Copper catalysts in combination with nitroxyl radicals[5] such as TEMPO,[6] 9-azabicyclo[3.3.1]nonane *N*-oxyl (ABNO),[7] or 2-azaadamantane *N*-oxyl (AZADO)[8] as co-oxidants have been applied in aerobic oxidations. However, most reported copper-catalyzed aerobic oxidations have been performed under homogeneous conditions, which inevitably resulted in poor recyclability of the metal catalyst. Switching from homogeneous catalysts to heterogeneous ones provides a potential solution to this problem.[9] Indeed, some heterogeneous copper catalysts, including Cu–Mn oxides/carbon,[10] Cu(II)/metal–organic framework,[11] Cu(II)/SiO$_2$,[12] CuFe$_2$O$_4$,[13] Cu(II)/β-cyclodextrin,[14] and Cu(II)/polymer[15] catalysts, have been developed, but these show several drawbacks, such as requirements for high oxygen pressures, toxic solvents, or bases. Therefore, the development of new heterogeneous copper catalysts for the aerobic oxidation of alcohols remains a significant challenge.

We recently developed a polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported triazine-based polyethyleneamine second-generation dendrimer (PS–PEG-TD2) (Scheme 1, a), and we produced a polymer-supported copper(II) catalyst (PS–PEG-TD2–CuSO$_4$) by treating this material with copper(II) sulfate. The supported copper catalyst efficiently promoted the Huisgen 1,3-dipolar cycloaddition of alkynes with organic azides, with high recyclability.[16] As a continuation of our efforts in the development of greener synthetic pathways for organic transformations,[17] our results prompted us to further explore other organic transformations using PS–PEG-TD2-supported copper catalysts. In this report, we describe the successful application of PS–

PEG-TD2–copper catalysts to the aerobic oxidation of alcohols in the presence of TEMPO. Benzylic, heterocyclic, and allylic alcohols bearing a wide range of substituents were efficiently converted into the corresponding aldehydes in good to excellent yields and with high selectivity. The catalyst could be readily recovered and reused four times without significant loss of its catalytic activity.

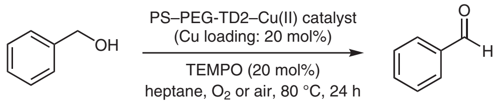


Scheme 1 (a) Structure of PS–PEG-TD2 resin and (b) preparation of the supported PS–PEG-TD2–Cu(II) catalysts

A series of polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported triazine-based polyethyleneamine dendrimer–copper catalysts [PS–PEG-TD2–Cu(II)] **A**–**D** were prepared according to our previous procedure.[16] Complexation of PS–PEG-TD2 with various copper salts [$Cu(OAc)_2{\cdot}H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2{\cdot}2H_2O$, or $CuSO_4{\cdot}5H_2O$] in methanol at room temperature for six hours afforded the corresponding PS–PEG-TD2–Cu(II) catalysts **A**–**D** (Scheme 1, b).[18] The copper loadings of catalysts **A**–**D** were determined to be 0.504, 0.402, 0.793, and 0.589 mmol/g, respectively, by ICP analysis.

Catalyst **A** (20.0 mol% Cu) was used for the oxidation of benzyl alcohol (**1a**) in the presence of TEMPO (20 mol%) in heptane under oxygen (1.0 atm) at 80 °C for 24 hours to give the desired benzaldehyde (**2a**) in 100% GC yield (Table 1, entry 1).[19] An absence of the catalyst or TEMPO under otherwise similar conditions resulted in poor production of the desired benzaldehyde (entries 2 and 3). When the reaction was conducted under air (1 atm) instead of oxygen, benzaldehyde (**2a**) was again obtained quantitatively (entry 4). Therefore, air was selected as the oxidant for subsequent investigations.[20] Reaction at 25 °C reduced the yield of **2a** to 37% (entry 5). PS-PEG-TD2–Cu(II) catalysts **B**–**D**, prepared from $Cu(NO_3)_2{\cdot}3H_2O$, $CuSO_4{\cdot}5H_2O$, and $CuCl_2{\cdot}2H_2O$, respectively, as copper sources, were also tested in the aerobic oxidation of benzyl alcohol (**1a**) (entries 6–8). Catalysts **B** and **C** were effective in the oxidation of benzyl alcohol and gave benzaldehyde (**2a**) in 100 and 91% yield, respectively (entries 6 and 7), whereas catalyst **D** was less effective, providing **2a** in 48% GC yield (entry 8). These results indicate that the counteranion of the copper salts affects the catalytic activity of the supported copper catalysts. As can be seen from Table 1, catalyst **A** derived from $Cu(OAc)_2$ (entry 4) and catalyst **B** derived from $Cu(NO_3)_2$ (entry 6) efficiently promoted the oxidation of benzyl alcohol to give benzaldehyde quantitatively.

Table 1 Screening of Conditions for the Aerobic Oxidation of Benzyl Alcohol[a]



1a **2a**

Entry	PS–PEG-TD2–Cu(II) catalyst	Oxidant	Temp (°C)	Yield[b] (%)
1	PS–PEG-TD2–Cu(OAc)$_2$ (**A**)	O_2	80	100
2	–	O_2	80	2
3[c]	PS–PEG-TD2–Cu(OAc)$_2$ (**A**)	O_2	80	6
4	PS–PEG-TD2–Cu(OAc)$_2$ (**A**)	air	80	100
5	PS–PEG-TD2–Cu(OAc)$_2$ (**A**)	air	25	37
6	PS–PEG-TD2–Cu(NO$_3$)$_2$ (**B**)	air	80	100
7	PS–PEG-TD2–CuSO$_4$ (**C**)	air	80	91
8	PS–PEG-TD2–CuCl$_2$ (**D**)	air	80	48

[a] Reaction conditions: BnOH (**1a**, 0.25 mmol), PS–PEG-TD2–Cu(II) catalyst (Cu loading: 20.0 mol%), TEMPO (20.0 mol%), heptane (2.0 mL), O_2 or air (1 atm), 24 h.
[b] Determined by GC analysis with biphenyl as internal standard.
[c] In the absence of TEMPO.

Recyclability of catalysts is an important aspect in relation to green sustainable processes and industrial applications. Catalysts **A** and **B** were examined for their recyclability in the aerobic oxidation of benzyl alcohol (**1a**). After completion of the reaction, the polymeric catalyst beads were separated from the reaction mixture by simple filtration, then washed with methyl *tert*-butyl ether[21] and air-dried carefully before reuse in subsequent runs. As shown in Figure 1, the activity of catalyst **A** showed no significant decrease during five consecutive runs, whereas the activity of catalyst **B** gradually decreased. These results suggest that catalyst **A**, derived from $Cu(OAc)_2$, is the best catalyst for the aerobic oxidation of benzylic alcohols.

A hot-filtration test was also conducted to confirm the heterogeneous nature of the PS–PEG resin-supported triazine-based dendrimer copper catalyst. After the aerobic oxidation of benzyl alcohol (**1a**) in the presence of catalyst **A** for two hours, the catalyst was removed from the reaction mixture by simple filtration, and the resulting filtrate was then heated at 80 °C for another 22 hours. No significant production of benzaldehyde (**2a**) was observed after removal of the catalyst (50% yield after two hours; 51% yield after 24 hours) (Figure 2). Moreover, ICP analysis of the filtrate after the first reaction showed that only traces (0.086%) of copper species were leached to the solution. These results clearly confirm that the PS–PEG resin-supported triazine-based dendrimer copper catalyst served as a heterogeneous catalyst in the aerobic oxidation.

Having the optimal catalyst and conditions in hand,[22] we examined the aerobic oxidation of various benzylic, heterocyclic, and allylic alcohols (Scheme 2). The reaction of benzylic alcohols bearing electron-donating or electron-withdrawing groups in the *para* position afforded the corresponding aldehydes **2b–l** in good to excellent yields. Various functional groups such as halo, ester, or nitro groups were also tolerated under the catalytic conditions. Substituents in the *meta* or *ortho* positions did not affect the reaction, and products **2m–p** were obtained in excellent yields. Piperonyl alcohol (1,3-benzodioxol-5-ylmethanol) and 2-

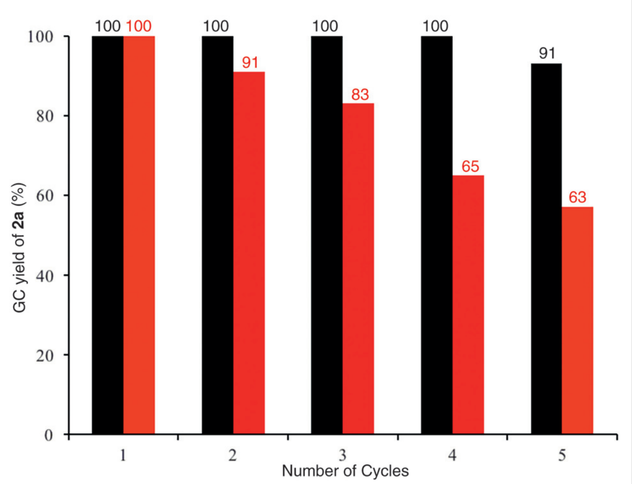


Figure 1 Activity of PS–PEG-TD2–Cu(II) catalysts **A** (black) and **B** (red) in recycling experiments for aerobic oxidation of benzyl alcohol (**1a**)

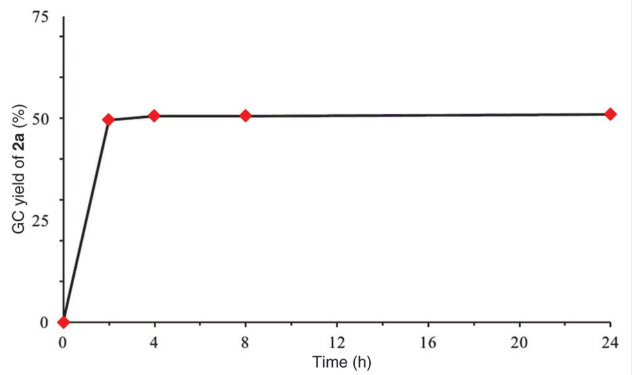
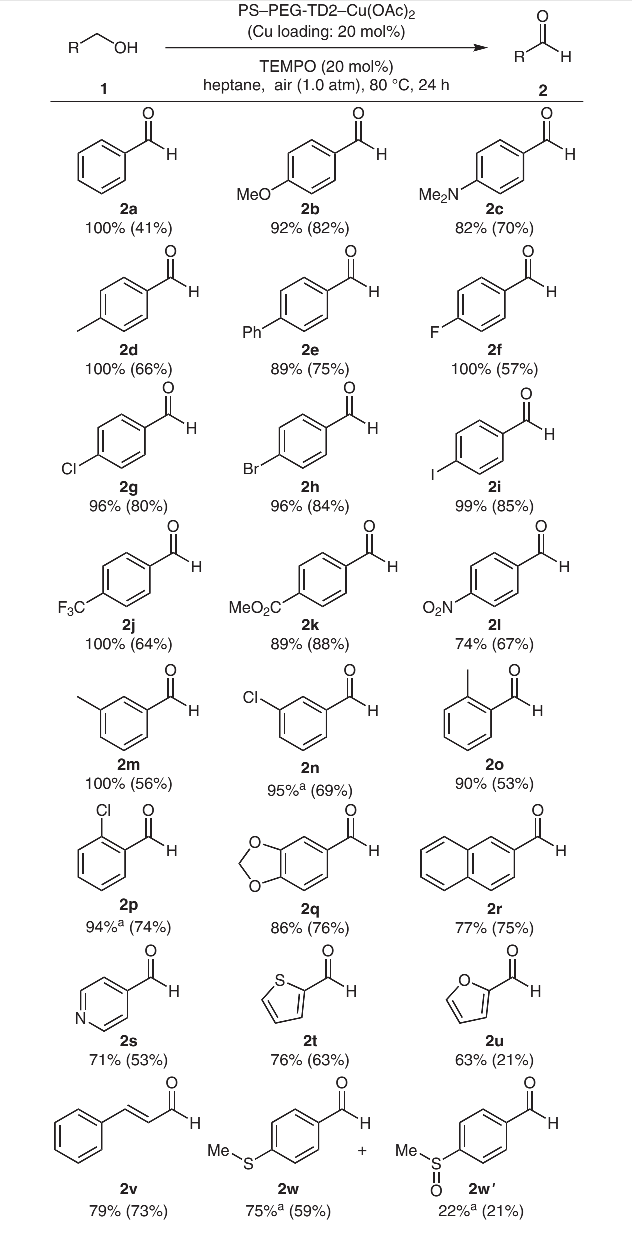


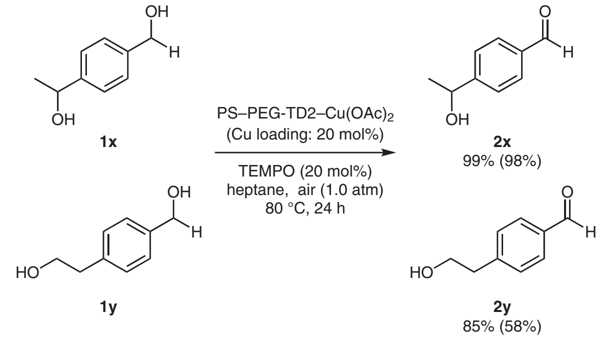
Figure 2 Hot-filtration test for the aerobic oxidation of benzyl alcohol (**1a**) with catalyst **A**. The catalyst was removed from the reaction mixture at 80 °C after reaction for 2 h. The resulting filtrate was further stirred at 80 °C.



Scheme 2 Substrate scope for the oxidation of alcohols. *Reaction conditions*: alcohol **1** (0.25 mmol), PS–PEG-TD2–Cu(OAc)$_2$ (Cu loading: 20.0 mol%), TEMPO (20.0 mol%), heptane (2.0 mL), air (1 atm), 24 h. Unless stated otherwise, yields were as determined by GC analysis with an internal standard; isolated yields are given in parentheses. [a] Determined by ^{1}H NMR analysis with an internal standard.

naphthylmethanol also reacted to afford aldehydes **2q** and **2r** in 86 and 77% yield, respectively. Heteroaromatic and cinnamyl alcohols were also converted into their corresponding aldehydes **2s–v** in 63–79% yield. In the case of 4-(methylsulfanyl)benzyl alcohol, the oxidation of the sulfide group to a sulfoxide proceeded concurrently under the catalytic conditions, giving aldehydes **2w** and **2w'** in 75 and 22% yield, respectively.

3-Phenyl-1-propanol and 1-phenylethanol were also submitted to the standard catalytic conditions. However, the aerobic oxidations were sluggish (5% and 15% GC yield, respectively). The results indicate that aliphatic alcohols and secondary alcohols are not applicable for the aerobic oxidation using PS–PEG-TD2–Cu(OAc)$_2$. In fact, when 4-(1-hydroxyethyl)benzylalcohol (**1x**) and 4-(2-hydroxyethyl)benzylalcohol (**1y**) were exposed to the standard catalytic conditions, the oxidation of the primary benzylic alcohols proceeded selectively to give 4-hydroxyethylbenzaldehydes **2x** and **2y** in 99 and 85% yield, respectively.



Scheme 3 Selective oxidation of primary benzylic alcohols. *Reaction conditions*: alcohol **1** (0.25 mmol), PS–PEG-TD2–Cu(OAc)$_2$ (Cu loading: 20.0 mol%), TEMPO (20.0 mol%), heptane (2.0 mL), air (1 atm), 24 h. Unless stated otherwise, yields were as determined by ^{1}H NMR analysis with an internal standard; isolated yields are given in parentheses.

In summary, an aerobic selective oxidation of alcohols to aldehydes by using PS–PEG resin-supported triazine-based dendrimer–copper complexes [PS–PEG-TD2–Cu(II)] has been developed. PS–PEG-TD2–Cu(OAc)$_2$ efficiently catalyzed the aerobic oxidation of primary benzylic alcohols to aldehydes in the presence of a catalytic amount of TEMPO. Various benzylic alcohols bearing a wide range substituents with various electronic properties and functionalities underwent aerobic oxidation to give the corresponding aldehydes in excellent yields. Heteroaromatic and cinnamyl alcohols were also suitable reactants for this transformation. In the aerobic oxidation of benzyl alcohol, the catalyst was recovered by simple filtration and reused four times without significant loss of its catalytic activity. Efforts to extend the range of applications of our supported copper catalysts to the other transformations are currently ongoing in our laboratory.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591981 and from the author.

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(18) **Synthesis of PS–PEG-TD2–Cu(II) Complexes A–D**
A mixture of PS–PED-TD2 (1.0 g) and the appropriate copper salt (1.0 mmol) in MeOH (10 mL) was stirred at r.t. for 6 h. The mixture was then filtered, and the resulting resin beads were washed with MeOH (10 × 10 mL) and dried in vacuo overnight. The copper loadings of the catalysts were determined by ICP–AES analysis.

(19) We investigated the solvent effect (toluene, H_2O, CH_3CN, and THF) on the aerobic oxidation of benzyl alcohol under the standard conditions. The aerobic oxidation in toluene and H_2O proceeded well to give benzaldehyde (**2a**) in 100 and 83% GC yield, respectively, while the reactions in CH_3CN and THF were sluggish (56 and 9% GC yield, respectively). In addition, ICP analysis for the recovered catalyst from the reaction in H_2O showed that 32% of the copper species leached into the solution during the reaction. On the basis of these results, we selected heptane for the further investigation.

(20) We monitored the formation of benzaldehyde in the aerobic oxidation of benzyl alcohol under O_2 and air. Similar reaction rates were observed under O_2 and air. Under O_2: 64% GC yield (2 h), 83% GC yield (4 h), 89% GC yield (8 h), 90 % GC yield (12 h). Under air: 52% GC yield (2 h), 79% GC yield (4 h), 87% GC yield (8 h), 96% GC yield (12 h).

(21) We also tested various solvents for washing the recovered catalyst. MTBE was an effective solvent to extract the organic materials and keep the copper content in the polymer matrix.

(22) **Synthesis of Aldehydes 2a–y; General Procedure**
A mixture of catalyst PS–PEG-TD2–Cu$(OAc)_2$ (100 mg, 0.05 mmol Cu), BnOH (**1a**, 27.0 mg, 0.25 mmol), and TEMPO (7.8 mg, 0.05 mmol) in heptane (2.0 mL) was stirred at 80 °C for 24 h under air (1 atm). The mixture was then cooled and filtered, and the resulting solid material was washed with Et_2O (3 × 2 mL). The organic phases were combined, concentrated to a volume of 2 mL, and the internal standard was added to determine the GC yield. The crude product was purified by column chromatography [silica gel, hexane–Et_2O (99:1)]. In the formation of some benzaldehydes, low isolated yields were observed because of instability of the benzaldehydes on silica gel.

Benzaldehyde (2a)
Colorless oil; yield: 10.8 mg (41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1 H), 7.89 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.56–7.52 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 136.4, 134.5, 129.7, 129.0.