A Highly Efficient Bifunctional Catalyst CoO_x/tri-g-C_3N_4 for One-Pot Aerobic Oxidation–Knoevenagel Condensation Reaction

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Abstract: A highly efficient bifunctional catalyst of an s-triazine-based carbon-nitride-supported cobalt oxide is developed for the aerobic oxidation–Knoevenagel condensation tandem reaction of benzyl alcohol and malononitrile, whereby 96.4% benzyl alcohol conversion with nearly 100% selectivity towards benzylmalononitrile can be obtained in 6 h at 80 °C. The excellent catalytic performance derives from the high basicity of carbon nitride and strong redox ability of Co species induced by carbon nitride. The catalyst is also quite stable and can be reused without any regeneration treatment, whose product yield is only an 11.5% reduction after four runs.

Keywords: one-pot reaction; aerobic oxidation; Knoevenagel condensation; cobalt oxide; carbon nitride

1. Introduction

The development of alternative clean and efficient processes is one of the priorities for modern chemistry, since traditional chemical synthesis and the resulting large consumption of fossil energy have caused a series of environmental pollution problems, which are destroying our ecological environment. The one-pot procedure has raised extensive interest since it can simplify the synthetic routes and minimize the production waste and energy consumption [1–5]. The challenges for one-pot transformation involve the development of heterogeneous catalysts with different catalytically active sites that can promote different reactions simultaneously and independently while not interfering with each other [6–8].

Benzylmalononitrile is a key intermediate for the preparation of antimalarial, which has numerous applications in the fields of pharmaceutical, biological, and synthetic chemistry [9]. Benzylmalononitrile is traditionally prepared by Knoevenagel condensation of malononitrile and benzaldehyde, the latter of which is generally obtained from the selective oxidation of benzyl alcohol, since alcohol is readily available as compared with the corresponding aldehydes. Preparation of benzylmalononitrile through tandem aerobic oxidation–Knoevenagel condensation reaction can greatly improve the synthesis efficiency [10–15]. One-pot synthesis of the above tandem reaction has been achieved by several researchers, including Qi [16], Miao [17], and Yan [18]. However, developing a simple and efficient catalyst is still a big challenge, since the activation of molecular oxygen under mild conditions is very difficult, especially without a noble metal.

Graphitic carbon nitride is known as a solid base catalyst that is active for the Knoevenagel condensation of benzaldehyde and malononitrile [19–22]. Meanwhile, it is also an outstanding support for the transition metal oxides, since the redox catalytic ability of the oxides can be improved greatly due to their unique interaction with g-C_3N_4 [23–27]. Recently, s-triazine-based carbon
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nitride (tri-g-C₃N₄) has been found to be a more ideal solid base catalytic material than g-C₃N₄ because it has more uncondensed amino groups (-NH, -NH₂) in the structure as compared with g-C₃N₄ [27–31]. These uncondensed amino groups can also be employed as anchors for supporting transition metal oxides.

Herein, a bifunctional catalyst with both basic and redox properties has been designed by supporting CoOₓ on tri-g-C₃N₄. Due to the basic activity of tri-g-C₃N₄ and the enhanced redox ability of Co species, this catalyst has excellent catalytic activity in aerobic oxidation–Knoevenagel condensation tandem reaction of benzyl alcohol and malononitrile, without addition of any auxiliary reagents. The reasons for this remarkable catalytic activity of CoOₓ/tri-g-C₃N₄ are also elucidated.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1 shows XRD patterns of CoOₓ/tri-g-C₃N₄ with different CoOₓ contents, together with that of tri-g-C₃N₄. For tri-g-C₃N₄, in addition to the two diffraction peaks assigned to g-C₃N₄ with 2θ of 13.2° and 27.7°, peaks at 12.3°, 20.0°, 24.0°, 26.7°, 29.5°, and 32.2° can also be observed, which are ascribed to tri-g-C₃N₄, corresponding to its (100), (110), (200), (002), (102), and (210) crystal planes, respectively [32]. The characteristic diffractions of g-C₃N₄ decrease and later disappear, while the (100) and (002) diffractions of tri-g-C₃N₄ remain with the increase of CoOₓ loading, demonstrating the transformation of g-C₃N₄ to tri-g-C₃N₄. No obvious characteristic diffraction peak of CoOₓ can be identified due to the relatively small CoOₓ loading and its high dispersion.

![Figure 1. The XRD patterns of (a) tri-g-C₃N₄, (b) 1CoOₓ/tri-g-C₃N₄, (c) 3CoOₓ/tri-g-C₃N₄, (d) 5CoOₓ/tri-g-C₃N₄, and (e) 7CoOₓ/tri-g-C₃N₄.](image-url)

The generation of the tri-g-C₃N₄ structure was further confirmed by the FT-IR spectra, which is shown in Figure 2. An intense absorption peak at 808 cm⁻¹ corresponding to the breathing modes of the s-triazine units [32] can be observed for all the catalysts. Skeletal stretching vibrations together with bending vibrations of s-triazine or tri-s-triazine located at 1250–1700 cm⁻¹ also appeared in the spectra. The broad absorption band in the range of 3100–3300 cm⁻¹ belongs to the stretching vibration of uncondensed N–H. A significant shift of the N–H band can be detected, probably caused by the interaction between the N–H group and CoOₓ species.

The SEM images of the obtained catalysts are presented in Figure 3, where tri-g-C₃N₄ exhibits a block structure made up of irregular layered sheets. No clear differences in morphology were found after CoOₓ loading, signifying that CoOₓ did not destroy the tri-g-C₃N₄ structure. This was confirmed by N₂ adsorption measurements, with similar type III isotherms with H3 hysteresis loops shown for all of the catalysts (illustrated in Figure S1). The hysteresis loops are more evident for the supported catalysts, revealing the increase of interparticle voids after the CoOₓ support. Table 1 shows the specific
surface areas and total pore volumes of the catalysts. Both become larger after Co loading, probably due to the intercalation of Co species into the layered structure, resulting in more interparticle voids. However, when the Co loading is further increased, the pore channel of tri-g-C$_3$N$_4$ may be partially blocked, leading to a reduction in pore volume.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** FT-IR spectra of (a) tri-g-C$_3$N$_4$, (b) 1CoO$_x$/tri-g-C$_3$N$_4$, (c) 3CoO$_x$/tri-g-C$_3$N$_4$, (d) 5CoO$_x$/tri-g-C$_3$N$_4$, and (e) 7CoO$_x$/tri-g-C$_3$N$_4$.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** SEM images of (a) tri-g-C$_3$N$_4$, (b) 1CoO$_x$/tri-g-C$_3$N$_4$, (c) 3CoO$_x$/tri-g-C$_3$N$_4$, (d) 5CoO$_x$/tri-g-C$_3$N$_4$, and (e) 7CoO$_x$/tri-g-C$_3$N$_4$.

The thermogravimetric method was employed to analyze the thermal stability of CoO$_x$/tri-g-C$_3$N$_4$ catalysts in air atmosphere. The results are shown in Figure 4. CoO$_x$/tri-g-C$_3$N$_4$ catalysts are all stable below 400 °C; only a slight weight loss caused by the desorption of H$_2$O or CO$_2$ was observed at the temperature range of 20–200 °C. The thermal decomposition temperature decreased gradually with the CoO$_x$ loadings, indicating that their thermal stability was lowered by the Co loadings. The actual content of Co in the catalyst was calculated by the remaining weight after TGA experiments. As shown
in Table 1, these were quite close to the contents added. The slightly increased content was caused by the partial decomposition of the tri-g-C₃N₄ support during the final calcination.

Table 1. Textural and basic properties of tri-g-C₃N₄ and CoOₓ/tri-g-C₃N₄.

| Catalysts          | SBET (m²/g) | V₅₅₅ (cm³/g) | Pore Size (nm) a | Co Content (%) b | Amount of Base Sites (mmol/g) c |
|--------------------|-------------|--------------|------------------|------------------|-------------------------------|
| tri-g-C₃N₄         | 3           | 0.02         | 26.3             | –                | 3.25                          |
| 1CoOₓ/tri-g-C₃N₄   | 13          | 0.12         | 35.9             | 1.3              | 2.73                          |
| 3CoOₓ/tri-g-C₃N₄   | 13          | 0.13         | 37.9             | 2.9              | 2.62                          |
| 5CoOₓ/tri-g-C₃N₄   | 9           | 0.07         | 32.3             | 5.4              | 2.50                          |
| 7CoOₓ/tri-g-C₃N₄   | 12          | 0.10         | 32.2             | 7.6              | 2.40                          |

a Defined as 4V₅₅₅/SBET; b Weight percentage of Co obtained by thermogravimetric analysis (TGA); c obtained by neutralization titration.

Figure 4. TG thermograms of (a) 1CoOₓ/tri-g-C₃N₄, (b) 3CoOₓ/tri-g-C₃N₄, (c) 5CoOₓ/tri-g-C₃N₄, and (d) 7CoOₓ/tri-g-C₃N₄.

The XPS method was used to detect the chemical states of Co and O on the catalyst surface, the results of which are displayed in Figures S2 and S3. Two peaks at ~796 eV and ~780 eV appeared in Figure S2, which are attributed to the Co 2p₁/₂ and Co 2p₃/₂ spin orbits, respectively. The ~780 eV peak can be deconvoluted into two peaks, with peak positions of 780.8 eV and 782.2 eV, corresponding to Co³⁺ and Co²⁺ species, respectively [26,33,34]. The Co³⁺/Co²⁺ ratio after fitting is listed in Table 2. It can be clearly seen that the ratio increases initially with the increase of Co loading. After further increasing the loading of Co, the Co³⁺/Co²⁺ ratio decreases. When the Co loading reaches 5%, the Co³⁺/Co²⁺ ratio is the largest. A high concentration of Co³⁺ may lead to an increase in the number of chemically adsorbed oxygen species on the catalyst surface [27]. This is proven by the O₁s spectra illustrated in Figure S3, which can be fitted into two peaks, with peak positions of 532.5 eV and 531.5 eV, corresponding to the adsorbed oxygen species and surface lattice oxygen species, respectively [35,36]. The ratio of the adsorbed oxygen species to the surface lattice oxygen ones has the same change tendency as the ratio of Co³⁺ to Co²⁺. The surface-adsorbed oxygen (Oₐds) is usually located in surface defects and is easier to reduce [37–39], which is crucial for catalytic oxidation.

Table 2. XPS results of CoOₓ/tri-g-C₃N₄ catalysts.

| Catalysts          | Co 2p₃/₂ Peaks | O₁s Peaks |
|--------------------|---------------|-----------|
|                    | Co²⁺ (eV)     | Co³⁺ (eV) | Co³⁺/Co²⁺ | Oₐds (eV) | Oₐlatt (eV) | Oₐds/Oₐlatt |
| 1CoOₓ/tri-g-C₃N₄   | 782.4         | 780.8     | 0.60      | 532.4     | 531.2       | 0.46        |
| 3CoOₓ/tri-g-C₃N₄   | 782.2         | 780.8     | 0.84      | 532.8     | 531.5       | 0.60        |
| 5CoOₓ/tri-g-C₃N₄   | 782.4         | 780.8     | 1.63      | 532.9     | 531.7       | 1.11        |
| 7CoOₓ/tri-g-C₃N₄   | 782.4         | 780.8     | 1.31      | 532.8     | 531.6       | 0.84        |
The surface basicities of the catalysts were measured by acid–base neutralization titration in aqueous solution, since the reactions investigated here are carried out in the liquid phase. The results are shown in Table 1. A large amount of basic sites were detected on tri-g-C$_3$N$_4$ surface despite its small specific surface area. This was because of the swelling effects in the liquid phase, which was also found on sulfonated carbon catalysts [40]. The amount of basic sites decreased with the Co loadings due to the interaction between the N-H group and CoO$_x$ species. However, the reduction was not too big in the range of present CoO$_x$ content. Basic sites measuring 2.40 mmol/g still remained on the 7CoO$_x$/tri-g-C$_3$N$_4$ catalyst, which was larger than those on pristine g-C$_3$N$_4$ [19].

2.2. Catalytic Performance

2.2.1. Aerobic Oxidation of Benzyl Alcohol

Aerobic oxidation of benzyl alcohol was conducted over CoO$_x$/tri-g-C$_3$N$_4$ catalysts, as well as tri-g-C$_3$N$_4$. The results are listed in Table 3. It can be seen that tri-g-C$_3$N$_4$ is not active for the oxidation, indicating that redox active sites come from the supported CoO$_x$ species. The activity increased sharply with the CoO$_x$ loadings, reaching the maximum and then decreasing slowly with further increases of the amount of CoO$_x$. 5CoO$_x$/tri-g-C$_3$N$_4$ has the best activity. The excellent redox catalytic ability can be attributed to the high chemisorbed oxygen species on the surface, since they are thought to be the most active oxygen species in the oxidation reaction, which can promote the formation of oxygen vacancies, as well as enhance the exchange of gaseous oxygen molecules and adsorbed oxygen molecules on the catalyst surface, thus promoting the oxidation reaction [41–43]. This can be proven by the XPS results in Table 2, which indicate that the change in activity with the Co loadings has the same trend as in the adsorbed oxygen-to-lattice oxygen ratio (O$_{ads}$/O$_{latt}$).

| Catalysts          | Aerobic Oxidation | Knoevenagel Condensation |
|--------------------|-------------------|--------------------------|
|                    | Time (h)          | Conversion (%)           | Time (h) | Conversion (%) |
| tri-g-C$_3$N$_4$   | 3.0               | 2.0                      | 0.5      | 76            |
| 1CoO$_x$/tri-g-C$_3$N$_4$ | 3.0               | 49.9                     | 0.5      | 74            |
| 3CoO$_x$/tri-g-C$_3$N$_4$ | 3.0               | 63.0                     | 0.5      | 72            |
| 5CoO$_x$/tri-g-C$_3$N$_4$ | 3.0               | 87.6                     | 0.5      | 71            |
| 7CoO$_x$/tri-g-C$_3$N$_4$ | 3.0               | 79.3                     | 0.5      | 70            |

2.2.2. Knoevenagel Condensation of Benzaldehyde and Malononitrile

The catalytic activities of the CoO$_x$/tri-g-C$_3$N$_4$ catalysts for the Knoevenagel condensation of benzaldehyde and malononitrile were also evaluated, together with that of tri-g-C$_3$N$_4$. All were very active for the condensation; nearly 100% conversion of benzaldehyde was obtained with the same reaction condition as oxidation (80 °C, 3 h). This can be ascribed to the abundant uncondensed amino groups (–NH, –NH$_2$) in the structure of tri-g-C$_3$N$_4$. Table 3 summarizes their catalytic activities at the lower temperature of 60 °C. It can be seen that the activity decreased with the CoO$_x$ loading, which can be ascribed to the reduction of basic sites, since Knoevenagel condensation is a typical base-catalyzed reaction. However, the decrease in activity is not as evident. The possible reason is that the reduction of basic sites was small, resulting in sufficient active sites remaining for catalyzing Knoevenagel condensation.

2.2.3. Oxidation–Condensation Tandem Reaction

The catalytic performances of CoO$_x$/tri-g-C$_3$N$_4$ catalysts towards one-pot aerobic oxidation–Knoevenagel condensation tandem reaction were evaluated, the results of which are summarized in Table 4. All were active for the tandem reaction. It can be seen that the conversion of benzyl alcohol increases with the CoO$_x$ loading, reaches the maximum at 5CoO$_x$/tri-g-C$_3$N$_4$, then
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decreases with further increases of the CoOx content. The trend for activity is exactly the same as that
of the oxidation reaction, owing to the much faster rate of condensation as compared with that of
oxidation. No intermediates benzaldehyde were found in any cases, indicating the oxidation is the
rate-determined step. The benzyl alcohol conversion also increased with the reaction time, and 96.4%
yield of benzylmalononitrile was obtained in 6 h over 5CoOx/tri-g-C3N4. The excellent catalytic
performance could be due to its dual function—the redox ability of supported CoOx species combined
with the basic sites retained in the tri-g-C3N4 support, which was confirmed by the above results of
individual oxidation and condensation reactions.

Table 4. Catalyst activity of tandem aerobic oxidation–Knoevenagel condensation reaction.

| Catalysts           | Time (h) | Conversion of A (%) | Yield of C (%) |
|---------------------|----------|---------------------|----------------|
| tri-g-C3N4          | 6        | 2.1                 | 1.9            |
| 1CoOx/tri-g-C3N4    | 3        | 43.9                | 43.9           |
| 3CoOx/tri-g-C3N4    | 6        | 65.5                | 65.5           |
| 5CoOx/tri-g-C3N4    | 3        | 85.5                | 85.5           |
| 7CoOx/tri-g-C3N4    | 3        | 96.4                | 96.4           |

It can also be seen that the conversion in individual oxidation over 5CoOx/tri-g-C3N4 at 3 h (87.6%)
is very close to that in the tandem reaction (83.2%), indicating that the two types of active sites in
5CoOx/tri-g-C3N4 would not interfere with each other during the tandem reaction.

The reusability of 5CoOx/tri-g-C3N4 in the aerobic oxidation–Knoevenagel condensation tandem
reaction was also investigated. After the reaction, the catalyst was filtered out from the reaction
liquid and then dried for the repeatability test. The results are shown in Figure 5. The conversion
of benzyl alcohol decreased continuously but slowly from 96.4% to 84.9% after three regeneration
processes, while the selectivity remained intact, indicating that 5CoOx/tri-g-C3N4 is quite stable in the
liquid-phase tandem reactions.

Figure 5. Recycling of 5CoOx/tri-g-C3N4 catalyst in the aerobic oxidation–Knoevenagel condensation
tandem reaction.
Table 5 summarizes the catalytic behavior over various catalysts for this tandem aerobic oxidation–Knoevenagel condensation reaction, which has been reported in previous literature. The high yield of benzylmalononitrile was obtained over our present catalyst under mild reaction conditions, without the use of expensive noble metals, giving it advantages over most of the catalysts reported before. Since Co$_3$O$_4$/C$_3$N$_4$ composites are active for aerobic oxidation of various aromatic alcohols bearing either electron-withdrawing groups or electron-donating groups [27], the present catalyst is believed to be applicable for aerobic oxidation–Knoevenagel condensation of various aromatic alcohols besides benzyl alcohol.

| Catalyst | Oxidant | Temperature (°C) | Time (h) | Conversion (%) | Yield (%) | Ref. |
|----------|---------|-----------------|---------|----------------|----------|-----|
| Au@Cu(II)-MOF | Air | 110 | 15 + 7 | 99 | 99 | [10] |
| OMS-2-SF | O$_2$ | 85 | 9 + 0.5 | 99.5 | 84.5 | [11] |
| Pd/LS-AT-OH | O$_2$ | 85 | 9 + 2 | 89.6 | 88.3 | [12] |
| Pd$_3$/Au$_5$/LDH | O$_2$ | 80 | 1.5 + 1 | 99 | 98.0 | [13] |
| UiO-66-Ru | O$_2$ | 80 | 1 + 5 | 100 | 89.3 | [14] |
| Pd/COF-TPPA-Py | O$_2$ | 80 | 4 + 1.5 | 98 | 98 | [15] |
| Au@MIL-53(NH$_2$) | O$_2$ | 100 | 100 | 99 | 99 | [16] |
| Cu$_3$TATAT-3 | O$_2$ | 75 | 12 | 95 | 95 | [17] |
| Fe$_3$Co$_3$@SiO$_2$@PEI@Ru(OH)$_2$ | O$_2$ | 110 | 22 | 98.6 | 90.2 | [18] |
| 5CoO$_x$/tri-g-C$_3$N$_4$ | O$_2$ | 80 | 6 | 96.4 | 96.4 | Present work |

Note: "m + n" means step-by-step reaction without separation of intermediate benzaldehyde.

3. Materials and Methods

3.1. Catalyst Preparation

The s-triazine-based g-C$_3$N$_4$ was synthesized as follows: 5 g melamine was dispersed in 30 mL ethylene glycol to obtain a saturated solution. Hereafter, 60 mL 0.1 M HNO$_3$ solution was added and stirred for 1 h at room temperature. The resulting mixture was filtered and washed three times with ethanol to remove the remaining nitric acid and ethylene glycol. Afterward, the mixture was dried at 120 °C and put into a covered ceramic crucible, heated under air flow at 5 °C/min up to 400 °C, and maintained for 2 h. The resulting product was cooled and grounded into powder.

The tri-g-C$_3$N$_4$ supported CoO$_x$ catalysts were synthesized as follows: 1 g obtained tri-g-C$_3$N$_4$ was put into an aqueous solution with a calculated content of Co(NO$_3$)$_2$·6H$_2$O. The mixture was stirred for 1 h at room temperature. After drying at 120 °C, the resulting solid was calcined under air flow at 2 °C/min up to 300 °C and maintained for 3 h. The obtained product was designated as yCoO$_x$/tri-g-C$_3$N$_4$, where y stands for the weight percentage of Co added.

3.2. Characterization of Catalyst

X-ray diffraction (XRD) was carried out on a D2 PHASER X-ray diffractometer (Brucker, Madison, WI, USA) using nickel-filtered Cu-K$_\alpha$ ($\lambda = 0.15418$ nm) at 40 kV and 30 mA in the range of 10°–80°. Fourier transform infrared spectra (FT-IR) were measured on a Nicolet iS10 spectrometer (ThermoFisher, Waltham, MA, USA). Scanning electron microscopy (SEM) was recorded on a Phenom Prox and by field-emission scanning electron microscopy (Ultra 55, Zeiss, Germany) with an acceleration voltage of 20.0 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Perkin-Elmer PHI 5000C spectrometer (Perkin-Elmer, Boston, MA, USA) using Mg K$_\alpha$ radiation (hv = 1253.6 eV) as the excitation source. The C$_{1s}$ peak at 284.6 eV was used as the reference of the binding energy. The N$_2$ adsorption isotherms were measured on a Micromeritics ASAP 2000 instrument (Micromeritics, Atlanta, GA, USA) at −196 °C. Specific surface areas of the catalysts were calculated by BET method and pore volumes were calculated by one-point method. Thermogravimetric (TG) analysis was carried out on a thermal analyzer TGA8000 (Perkin-Elmer, Waltham, MA, USA) under the inflow of air, with a ramp rate of 10 °C/min from 20–900 °C.
3.3. Basicity Measurement

The surface density of base sites was evaluated by neutralization titration. Typically, a 20 mg sample was put into 10 mL 0.05 mol/L aqueous hydrochloric acid solution. The mixture was stirred for 30 min under N₂ flow. The solid was then removed by filtration and the remaining solution was immediately titrated with a 0.05 mol/L sodium hydroxide solution using phenolphthalein as the indicator.

3.4. Catalyst Evaluation

Knoevenagel condensation. In a round bottom flask, 1 mmol benzaldehyde, 2 mmol malononitrile, 10 mL N,N-dimethylformamide, and 50 mg catalyst were added in this order and stirred at 60 °C for 0.5 h with reflux. The reaction products were analyzed using a GC9560 gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.3 μm).

Oxidation of benzyl alcohol. 0.1 g catalyst, 0.25 mmol benzyl alcohol, and 20 mL N,N-dimethylformamide were added into a round-bottom flask. The mixture was reacted at 80 °C for 3 h with an O₂ stream of 50 mL/min under magnetic stirring. The products were analyzed using a GC9560 gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.3 μm).

Oxidation–condensation tandem reaction. The tandem reaction of benzyl alcohol and malononitrile was carried out in a round-bottom flask equipped with a reflux condenser under magnetic stirring. Typically, 0.1 g catalyst was added into the mixture of 0.25 mmol benzyl alcohol, 0.5 mmol malononitrile, and 20 mL N,N-dimethylformamide. The reaction was performed at 80 °C for 3 h and 6 h, with an O₂ flow of 50 mL/min. Products were analyzed using a GC9560 gas chromatograph equipped with a SE-30 capillary column (30 m × 0.25 mm × 0.3 μm).

4. Conclusions

A bifunctional catalyst was prepared by supporting cobalt oxide on s-triazine-based carbon nitride. The abundant ammonia species (especially –NH and –NH₂ groups) on the support not only act as basic active sites for Knoevenagel condensation but also enhance the catalytic activity of Co species in oxidation reactions. This catalyst exhibits excellent catalytic performance in the aerobic oxidation–Knoevenagel condensation tandem reaction without any auxiliary reagent and can easily be reused by simple filtration, for which the activity reduces by only 11.5% after four circles. The catalyst has fantastic potential for applications in industrial production.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/712/s1: Figure S1: N₂ adsorption/desorption isotherms of (a) tri-g-C₃N₄, (b) 1CoOₓ/tri-g-C₃N₄, (c) 3CoOₓ/tri-g-C₃N₄, (d) 5CoOₓ/tri-g-C₃N₄, and (e) 7CoOₓ/tri-g-C₃N₄. Figure S2: XPS spectra of Co₂p in the 1CoOₓ/tri-g-C₃N₄, 3CoOₓ/tri-g-C₃N₄, 5CoOₓ/tri-g-C₃N₄, and 7CoOₓ/tri-g-C₃N₄. Figure S3: XPS spectra of O₁s in the 1CoOₓ/tri-g-C₃N₄, 3CoOₓ/tri-g-C₃N₄, 5CoOₓ/tri-g-C₃N₄, and 7CoOₓ/tri-g-C₃N₄.

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