Cobalt Vanadium Oxide Supported on Reduced Graphene Oxide for the Oxidation of Styrene Derivatives to Aldehydes with Hydrogen Peroxide as Oxidant

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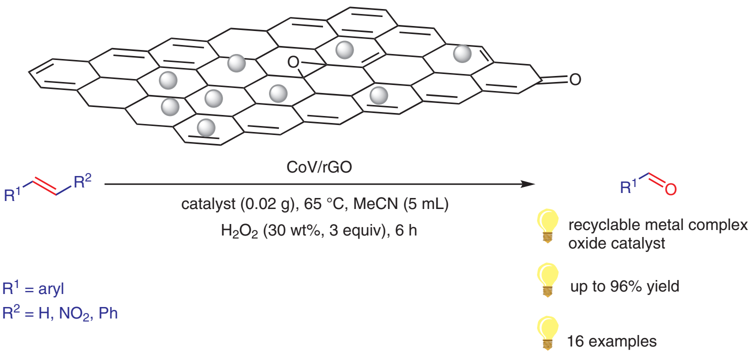

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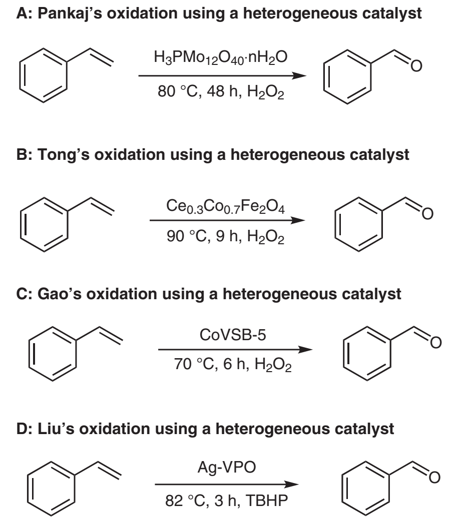
Abstract Cobalt vanadium oxide supported on reduced graphene oxide showed excellent performance in the oxidation of styrene derivatives to the corresponding aldehydes with hydrogen peroxide as oxidant. An electron-donating group at the *para*-position of the aromatic ring facilitates the formation of the corresponding aldehyde. Compared with conventional methods, the newly designed heterogeneous catalytic system offers a promising prospect because of its economic applicability and environmental friendliness.

Key words cobalt vanadium oxide, reduced graphene oxide, styrene oxidation, hydrogen peroxide, styrene derivatives, aldehydes

The oxidation of olefins occupies an important position in academic research and industrial utilization. Numerous fine chemicals such as epoxides, diols, carbonyl compounds, and aldehydes can be synthesized through this oxidation reaction. Benzaldehyde, as a versatile fine chemical, has attracted great interest due to its widespread application in the manufacture of perfumes, dyestuffs, pharmaceuticals, and agrochemicals.[1] Benzaldehyde is usually produced by hydrolysis of (dichloromethyl)benzene, and it can be also prepared through oxidation of toluene.[2] However, both processes can cause serious pollution, which does not satisfy the desire for environmentally friendly chemistry. Traces of chlorine-containing contaminants, which are often present after the hydrolysis of (dichloromethyl)benzene, are unacceptable in commodity chemicals; furthermore, copious waste is generated in this process. Oxidation of toluene is usually carried out in organic solvents, which are environmentally undesirable.[3] In view of producing benzaldehyde by a green method, increasing attention has been paid to the green oxidation of styrene to benzaldehyde.

The key to the success of this reaction is to use an efficient catalyst that activates H_2O_2 to oxidize styrene. In recent years, tremendous efforts have been dedicated to solving this problem, and many researches have been reported in this field. The catalysts are generally divided into two broad categories: homogeneous catalysts[4] and heterogeneous catalysts.[5] Homogeneous catalysts are less attractive on account of difficulties in separating them from their reaction mixtures. Compared with homogeneous catalysts, heterogeneous catalysts can be easily isolated from the reaction mixture. Therefore, considerable attention has been devoted to the use of heterogeneous catalysts for the green oxidation of styrene. Various heterogeneous catalysts have been applied to the oxidation of styrene,[6] including heteropoly acids, cerium-doped cobalt ferrites, molecular sieves,



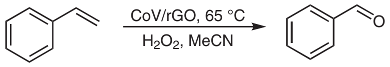
Scheme 1 Examples from the literature of the use of heterogeneous catalysts

and silver-doped vanadium phosphorus oxides (Scheme 1). Some catalysts are not sufficiently active to catalyze the transformation of styrene into benzaldehyde, or they cannot be reused with comparable properties to the fresh catalyst. Hence, finding a better heterogeneous catalyst is still a serious challenge and there is an urgent need to improve both the performance and reusability of catalysts.

Graphene, a honeycomb-like planar sheet of sp^2 carbon atoms in a hexagonal array, exhibits outstanding properties in terms of its electrical conductivity, thermal conductivity, and thermostability.[7] Graphene oxide (GO) is usually prepared by chemical treatment of graphene with $KMnO_4/H_2SO_4$ according to the modified method of Hummers and Offeman.[8] The surface of GO contains an abundance of oxygen-containing groups (hydroxy, carboxy, carbonyl, and epoxide functional groups). As a result, GO is hydrophilic and can be readily exfoliated in water to form a stable colloidal suspension. GO can be reduced to give reduced GO (rGO),[9] which has comparable properties to pure graphene, but which retains functional groups.[10] These remaining groups on the surface of rGO can act as anchoring sites for metals, providing rGO with promising performance in the catalytic field. Although various metal nanoparticles supported on rGO have been studied in the field of catalysis,[11] few researches on metal complex oxides have been reported.[12]

Inspired by previous reports,[5c,6b,e,f] we designed CoV/rGO and NiV/rGO composites that we prepared by using a mild and environmentally friendly hydrothermal method. Surprisingly, these composites efficiently catalyzed the oxidation of styrene to benzaldehyde. In addition, a wide range of olefins could be transformed into aldehydes by using CoV/rGO as catalyst. The heterogeneous catalyst could be recycled seven times without a significant decrease in its catalytic performance.

Table 1 Optimization of the Reaction Conditions[a]



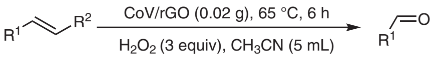
Entry	Catalyst	H_2O_2 (equiv)	Conversion[b] (%)	Yield[b] (%)
1	rGO	3	trace	trace
2	CoV	3	81	71
3	CoO	3	21	19
4	NiO	3	18	13
5	V_2O_5	3	70	42
6	NiV	3	77	60
7	CoV/rGO	3	98	91
8	NiV/rGO	3	90	82
9[c]	CoV/rGO	3	20	15
10[d]	CoV/rGO	3	53	36
11[e]	CoV/rGO	3	84	67
12[f]	CoV/rGO	3	97	74[g]
13	CoV/rGO	2	67	61
14	CoV/rGO	4	99	89
15[h]	CoV/rGO	3	<63	<49
16[i]	rGO	3	9	3

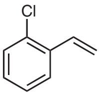
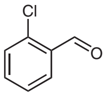
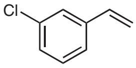
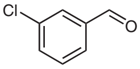
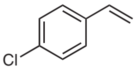
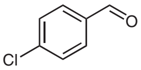
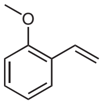
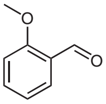
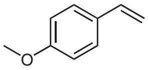
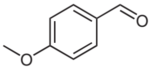
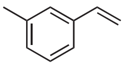
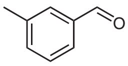
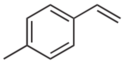
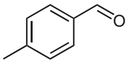
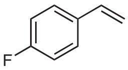
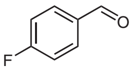
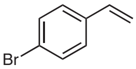
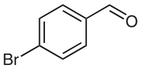
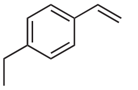
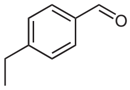
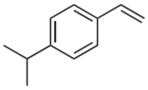
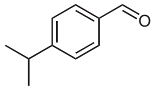
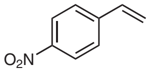
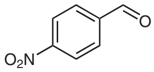
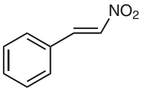
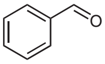
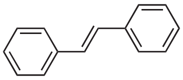
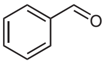
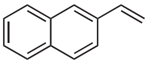
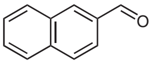
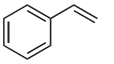
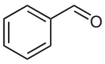
[a] Reaction conditions: styrene (1 mmol, 0.10 g), catalyst (0.02 g), MeCN (5 mL), 65 °C, 6 h.
[b] determined by GC.
[c] At 25 °C.
[d] At 50 °C.
[e] At 60 °C.
[f] At 70 °C.
[g] 21% of benzoic acid was detected.
[h] Solvents: EtOH, CH_2Cl_2, EtOAc, HOAc, or H_2O.
[i] At 80 °C.

In our preliminary experiments, we selected styrene as a model substrate to optimize the reaction conditions (Table 1). To identify the active components that actually influence the oxidation reaction, styrene was initially treated with various catalysts (Table 1, entries 1–8). The results revealed that rGO alone did not catalyze this oxidation (entry 1). The conversion of styrene and the yield of benzaldehyde were 81% and 71%, respectively, in the presence of cobalt vanadium oxide alone (entry 2), which were better results than those obtained with cobalt oxide or vanadium oxide alone (entries 3 and 5). This suggested that there was a synergistic effect between cobalt and vanadium. A similar tendency was observed with nickel vanadium oxide (entries 4–6). Interestingly, when we used rGO as a support, CoV/rGO and NiV/rGO showed better catalytic activities (entries 7 and 8) giving benzaldehyde in yields of 91% and 82%, respectively. This was attributed to the dispersion of active components on the rGO support, as confirmed by TEM analysis (Fig S5; Supporting Information). After identifying the most effective catalyst for the reaction, it was imperative to investigate the effect of temperature. The yield of benzaldehyde improved on raising the temperature from 25 °C to 65 °C (entries 7, 9–11). However, when the temperature was increased further to 70 °C, the yield decreased as a result of overoxidation of benzaldehyde to benzoic acid (entry 12). The use of three equivalents of hydrogen peroxide was found to be most suitable for the current catalytic system (entry 7); further increases in the amount of hydrogen peroxide did not show any positive effect (entry 14), whereas reducing the amount of hydrogen peroxide to two equivalents led to a drop in the yield (entry 13). Subsequently, a series of experiments were carried out in various solvents (entries 7, 15). The results showed that acetonitrile was the optimal solvent for this reaction and that other solvents produced inferior yields. This might be because the high dielectric constant of acetonitrile permits the various reaction phases to exist in a uniform condition, thereby increasing the efficiency of mass transfer.[13] The conversion of styrene and the yield of benzaldehyde were lower than expected when water, the solvent with the highest dielectric constant, was used. This is because the insolubility of styrene in water hinders contact between the substrate and oxidant.

The oxidation of various styrene derivatives over the solid CoV/rGO catalyst was studied under the optimal conditions, and the results are shown in Table 2. Surprisingly, we found that the position of substituent groups had a significant effect on the yield of the desired product. When the substituent groups were in the *para*-position, substrates were easily transformed, and more of the desired product was obtained (Table 2, entries 3, 5, and 7). However, when substituent groups were in the *ortho*- or *meta*-position, a lower yield was obtained (entries 1, 2, 4, and 6), especially when the substituents were in the *ortho*-position (entries 1 and 4). Furthermore, the nature of the substituent group also influenced the results of the oxidation. An electron-donating group was beneficial for the transformation of the substrate into the desire product, whereas an electron-withdrawing group decreased the conversion of the substituted styrene (entries 3, 5, and 7–13). Conjugation of the aromatic ring with an exocyclic double bond also increased the yield of the target product (entry 14).

Table 2 Extension of the Substrate Scope[a]



Entry	Substrate	Product	Yield[b] (%)
1			55
2			78
3			85
4			63
5			92
6			84
7			89
8			84
9			89
10			92
11			93
12			67
13			34
14			96
15			46
16			91

[a] Reaction conditions: substrate (1 mmol), MeCN (5 mL), CoV/rGO (0.02 g), H_2O_2 (3 equiv), 65 °C, 6 h.
[b] Isolated yield.

In consideration of pursuing practical applications, we investigated the stability and reusability of the CoV/rGO catalyst. After each experiment, the catalyst was separated from the products by centrifugation, washed twice with ethanol and deionized water, and dried at 60 °C before reuse in the next experimental run. The results of a recycling test performed under the optimal conditions for styrene oxidation are shown in Figure 1. It was clear that there were only marginal decreases in the conversion of styrene and in the yield of benzaldehyde after seven cycles of catalyst reuse. This demonstrated that the catalyst exhibited an outstanding performance in terms of its stability and reusability.

On the basis of a previous report,[14] we propose a plausible mechanism for the CoV/rGO-catalyzed oxidation of olefins with H_2O_2 (Scheme 2). Cobalt vanadium peroxide (**I**) is formed by the oxidation of H_2O_2 (Step 1). The active peroxide species then attacks the double bond of styrene and generates an intermediate species **II** (Step 2) that rapidly breaks down to give styrene oxide with regeneration of cobalt vanadium oxide (Step 3). Finally, the styrene oxide reacts with hydrogen peroxide to generate benzaldehyde (Step 4).

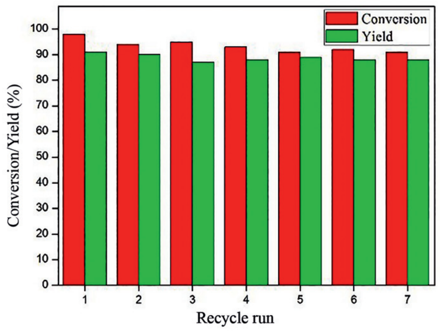
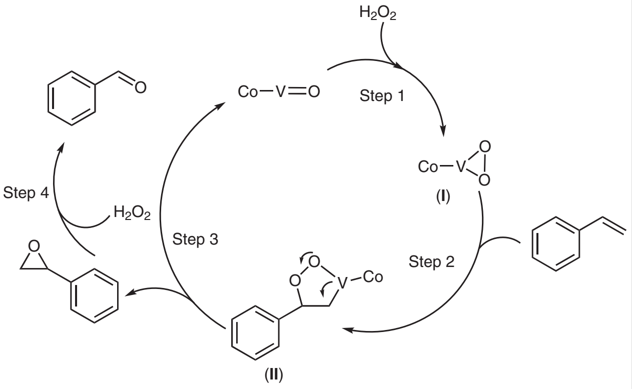


Figure 1 Recycling of the catalyst



Scheme 2 A plausible mechanism for the oxidation reaction with H_2O_2

In summary, we have successfully designed an economical, environmentally friendly, and efficient catalyst system for the selective oxidation of styrene derivatives to the corresponding aldehydes.[15] The CoV/rGO catalyst shows high performance in the preparation of aldehydes with H_2O_2 as a green oxidant. The newly developed system has a bright outlook for prospective applications in industry.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610630.

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(15) **Typical Procedure**
The oxidation of styrene derivatives was carried out in a 50 mL two-necked round-bottomed flask. Substrate (1 mmol) was stirred with the CoV catalyst (0.02 g) in MeCN (5.0 mL). 30 wt% H_2O_2 (0.34 g) was added slowly to the mixture, the temperature was increased to 65 °C, and the mixture was stirred for 6 h. The catalyst was separated by centrifugation and the product was extracted with EtOAc and sat. aq NaCl. The organic phase was dried (Na_2SO_4) and purified by column chromatography.
Benzaldehyde (Table 2, entry 16): Colorless liquid; to give a colorless liquid; yield: 91 mg (91%). ^1H NMR (500 MHz, $CDCl_3$); δ = 10.08 (s, 1 H), 7.98–7.91 (m, 2 H), 7.69 (t, J = 7.4 Hz, 1 H), 7.59 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$); δ = 191.87, 135.96, 133.98, 129.24, 128.53.