



Nanoshell carbon-supported cobalt catalyst for the aerobic oxidation of alcohols in the presence of benzaldehyde: An efficient, solvent free protocol

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ABSTRACT

A versatile, solvent free aerobic alcohol oxidation system has been established in the presence of benzaldehyde based on a heterogenous cobalt catalyst supported on nanoshell carbon (Co/NSC), which was prepared through the pyrolysis of a mixture of Co(II) phthalocyanine and phenol resin. The established system features equal efficiency toward both benzylic alcohols and aliphatic alcohols. The nanoshell carbon has been demonstrated to be a better supporting material for the present reaction than some other carbon materials, e.g., activated carbon. Mechanistic studies suggest that Co/NSC can catalyze the formation of oxidative intermediate peroxybenzoic acid as efficiently as homogeneous cobalt catalyst, and moreover, suppress the undesired Baeyer–Villiger side reaction. Co/NSC also exhibits good reusability, i.e., it can be reused for at least 10 times without significant loss of performance.

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1. Introduction

The oxidation of hydroxy group to corresponding carbonyl or carboxylic group is one of the most fundamental transformations in organic chemistry [1,2]. Although numerous methods have been developed over past decades, efficient, cost effective and environment friendly techniques are still highly sought-after [3]. Apparently, such techniques should be conducted in an aerobic and catalytic way [4,5]. And heterogenous catalysts are favored over homogeneous ones in terms of product purification and catalyst recovery [6,7]. Most of the reported aerobic oxidation methods are based on precious metals, however, their rarities and high costs make them impractical for large-scale industrial applications. Furthermore, those methods generally perform less efficiently when being applied to aliphatic alcohols, especially cyclic ones [7]. We herein report a nanoshell carbon-supported cobalt catalyst (Co/NSC) based aerobic oxidation system, which expediently oxidizes benzyl alcohols as well as linear and cyclic aliphatic alcohols at the same level of efficiency under solvent free conditions in the presence of benzaldehyde.

This research was inspired by the process of cobalt-catalyzed autoxidation of aldehydes, in which peracid intermediates are generated [8,9]. We postulated that the peracid intermediate can be utilized to efficiently oxidize alcohols under certain conditions. A similar system with ruthenium–cobalt bimetallic catalyst has been

reported by Murahashi et al. [10]. Their method enables rapid oxidation of alcohols under remarkably mild conditions; however, it involves the use of precious metal (RuCl_3), high loading of aldehyde (4 eq.), as well as large amount of solvent (0.2 M). Moreover, the catalyst used therein is homogeneous as Co(II) acetate (Co(II)Ac) dissolves in the solution. Our aim is to develop a heterogeneous system that eliminates the use of precious metal and reduces the use of aldehydes and solvents.

2. Experimental

2.1. Materials and characterization methods

All alcohol substrates, activated carbon (NORIT SX Plus), and other chemicals were obtained from commercial suppliers and were used as received. Transmission electron spectroscopy (TEM) was performed with a JEOL JEM-2010F microscope. Elemental analysis (EA) was conducted with a Perkin Elmer 2400 Series II for CHN, and a LECO VTF-900 for oxygen. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Perkin Elmer 5500-MT spectrometer. Electron probe microanalysis (EPMA) was carried out with a JEOL JXA-8200 electron probe micro-analyzer. Oxidation reactions were carried out using a SIBATA Chemist Plaza CP100 multi-reactor equipped with 30×200 mm sized test tubes as reaction vessels and separate magnetic stirrers. Samples were taken with a hypodermic syringe and diluted in acetone, and analyzed by a SHIMAZDU GCMS-QP2010 Plus, using a TC-FFAP capillary column ($30 \text{ m} \times 0.25 \text{ mm}$). Helium was used as carrier gas with a flow rate of 1.53 mL/min.

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The temperature program for all analyses is as follows: an oven temperature of 70 °C for 4 min, with a ramp rate of 10 °C/min to 200 °C for 30 min. Quantitative analysis was based on area normalization.

2.2. Preparation of nanoshell carbon-supported cobalt catalysts

Preparation of Co/NSC: 1 g of cobalt phthalocyanine was blended with 4.156 g of phenol resin in 300 mL of acetone in a glass flask. The materials were well dispersed by sonication and then acetone was removed by evaporation. After drying the residue under reduced pressure, the blend was heated to 800 °C under N₂ flow over 1 h and kept at 800 °C for 4 h. The obtained material was pulverized by ball milling to obtain small particles and was heat treated again.

Preparation of HCl-washed Co/NSC (wCo/NSC): 0.5 g of Co/NSC was dispersed in 200 mL of 37% HCl solution and was vigorously stirred overnight. After filtration, the carbon material was washed to neutral with deionized water. Such procedures were repeated twice. The resulted carbon was then dried under vacuum for 20 h.

Preparation of HNO₃-oxidized Co/NSC (oCo/NSC): 0.2 g of Co/NSC was heated under reflux in 100 mL of 40% HNO₃ solution for 12 h. Then the carbon material was filtered and rinsed to neutral with deionized water. The resulted oCo/NSC was dried under vacuum for 20 h. HNO₃-oxidized activated carbon (oAC) was prepared likewise.

2.3. General oxidation method

General oxidation method (2-octanol as an example): 5 mg of Co/NSC, 1.62 mL (10 mmol) of 2-octanol were charged into a test tube, followed with sonication for 20 s. The tube was then sealed and evacuated with a vacuum pump, followed by the attachment of an oxygen balloon. The reaction mixture was heated to 110 °C, using an aluminum block. 2.08 mL (20 mmol) of benzaldehyde was added portion wise over 4 h (25% per hour). After another 12 h reaction, the resulted mixture was analyzed with GC–MS.

3. Results and discussion

3.1. Nanoshell carbon characterization

Nanoshell carbon possesses shell-like carbon structures in the range of 20–50 nm and can be easily prepared through the pyrolysis of a mixture of transition-metal complex and polymer precursor [11–13]. In the process of pyrolysis, transition-metal is reduced to nano-particles with sizes less than 40 nm. After pulverization, the BET surface area of resulted carbon materials is generally between 200 and 400 m² g⁻¹. Co/NSC used in this study was prepared from a mixture of Co(II) phthalocyanine (Co(II)Pc) and phenol resin, with a cobalt content of ca. 4 wt% determined by EA and EPMA (Table 1). XPS result shows that cobalt only accounts for ca. 0.2 wt% on the surface (up to ca. 10 nm depth), indicating most of the cobalt particles are in the bulk. TEM images, shown in Fig. 1, reveal the formation of nanoshell carbon structures and the distribution of Co particles, whose sizes are less than 20 nm.

3.2. Optimization of alcohol oxidation conditions

In our preliminary screening of aldehydes, we found that peracids from aliphatic aldehydes tend to decompose immediately after formation rather than to react with alcohols in the absence of ruthenium. In contrast, benzaldehyde (BzH) forms a stabler and more oxidative peracid that is strong enough for alcohol oxidation without the help of ruthenium. Therefore, benzaldehyde was chosen as the peracid source in our following studies. The substrate

Table 1
Characterizations of pristine, HCl washed, and HNO₃ oxidized Co/NSC.

	Elemental analysis			
	C (%)	H (%)	N (%)	O (%)
Co/NSC	87.31	0.43	2.09	6.39
wCo/NSC	87.61	0.41	2.12	6.44
oCo/NSC	64.28	0.81	1.80	33.11
	XPS			
	C (%)	N (%)	O (%)	Co (%)
Co/NSC	90.45	1.04	8.30	0.20
wCo/NSC	85.92	0.97	13.11	0
oCo/NSC	75.42	1.93	22.65	0
	EPMA			
	C (%)	N (%)	O (%)	Co (%)
Co/NSC	92.35	2.21	1.43	4.01
wCo/NSC	93.21	2.32	1.49	2.99
oCo/NSC	78.10	2.30	19.32	0.19

2-octanol was generally used in our condition optimization investigations. The autoxidation of benzaldehyde proceeded smoothly in 1,4-dioxane, t-butanol and heptane; however, the solvents containing nitrogen or chlorine atom largely retarded the process. Nevertheless, all those results are inferior to that obtained under solvent free conditions in the conversion of 2-octanol. The temperature effect is shown in Fig. 2, generally the conversion of 2-octanol increases with temperature with predetermined amount of benzaldehyde. However, the selectivities to ketone product are affected by elevated temperature because of side reactions. Therefore, 110 °C was finally chosen as a trade-off between reaction rate and selectivity. The BzH loading effect is shown in Table 2. Upon fixed Co/NSC loading, BzH ranging from 1.25 equivalents to 2 equivalents were used to compare the respective alcohol conversion. It was found that 2 equivalents of BzH is enough to deliver full conversion of 2-octanol. In contrast, in the absence of catalyst, only 40% conversion of 2-octanol was obtained under identical reaction conditions. The optimized reaction condition was finally obtained for the quantitative oxidation of 2-octanol as shown in Table 3, entry 2. At 110 °C, in the presence of 5 mg of Co/NSC and 2 eq. of BzH added portion wise, 10 mmol of 2-octanol can be fully oxidized with excellent selectivity to ketone after 16 h reaction. Indeed, over 80% of BzH was converted to acid within 6 h; prolonged reaction time was adopted to ensure the full conversion of BzH. Without any catalyst, the BzH autoxidation was much slower, and more importantly, the conversion of alcohol was very low (entry 1).

3.3. The effect of the supporting material

To get an insight into the effect of nanoshell carbon on catalyst performance, we treated Co/NSC with HCl wash and HNO₃ oxidation to obtain wCo/NSC and oCo/NSC, respectively (see Table 1 for elemental characterization and Fig. 1 for TEM images). After the HCl wash, the total cobalt content was decreased by ca. 1 wt% and XPS detected no signal of cobalt, suggesting that the external or surface cobalt has been all removed by HCl. Interestingly, after the catalyst was oxidized with 40% HNO₃ under reflux, the bulk cobalt was almost fully extracted. These observations indicated that HNO₃ can reach much deeper than HCl into the carbon material, probably due to the difference in lipophilicity. Thus the structure feature of Co/NSC and the effect of HCl wash and HNO₃ oxidation can be simply illustrated as shown in Fig. 3. On the other hand, wCo/NSC exhibited a slightly reduced catalytic performance (Table 3, entry 3), while the performance of oCo/NSC largely declined (entry 4).

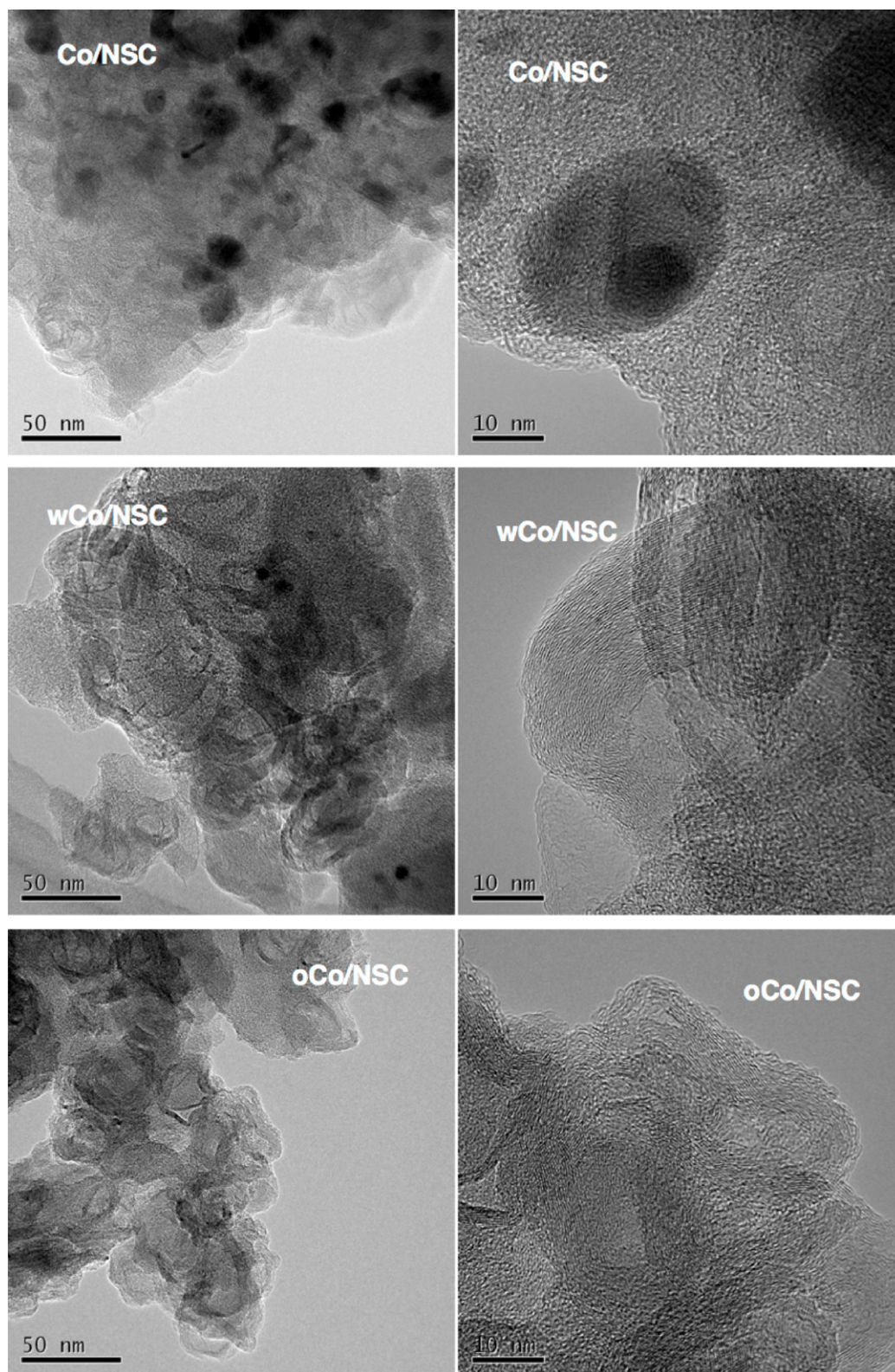


Fig. 1. TEM images of Co/NSC, wCo/NSC and oCo/NSC.

However, the alcohol conversion in the case of oCo/NSC is still better than that in the absence of catalyst. Moreover, the supported cobalt catalyst Co/NSC performed as well as homogeneous catalysts, Co(II)Ac (entry 5) and Co(II)Pc (entry 6) at the same amount of cobalt. Therefore, it can be concluded that not only the surface cobalt but also the cobalt encapsulated in the bulk are accessible to

BzH and the nanoshell carbon does show some positive effect on the alcohol oxidation.

Conventionally, cobalt has been loaded on activated carbon (AC) or carbon black via wet impregnation and subsequent reduction [14–19]. The preparation of Co/NSC is obviously simpler. Besides, the cobalt particles in Co/NSC are well dispersed in the bulk rather

Table 2
Effect of benzaldehyde loading.

Entry ^a	Catalyst	Amount of BzH (eq.)	BzH conv. (%)	2-Octanol conv. (%)
1	Co/NSC	1.25	97	75
2	Co/NSC	1.5	97	80
3	Co/NSC	2	100	96
4	–	1.25	92	39
5	–	1.5	82	30
6	–	2	84	40

^a General conditions: 2-octanol (10 mmol), Co/NSC (5 mg in entry 1–3), O₂ (balloon pressure), 110 °C, 16 h; BzH was added portionwise over 4 h.

than only on the surface, thus improved stability can be easily imagined. To study the actual stability of Co/NSC, we collected the catalyst by membrane filtration after a fresh use in the oxidation of 2-octanol and reused it under identical reaction conditions. The conversions of both 2-octanol and BzH were monitored after each run. As shown in Fig. 4, no significant loss of catalytic activity was observed in subsequent 9 runs, indicating the superior durability of Co/NSC. Moreover, it has been demonstrated that activated carbons are inappropriate to be used as supporting material for this type of reaction. As shown in entry 7, in the presence of AC, extremely low conversion (1%) of BzH was observed after 16 h reaction at 110 °C. So AC does not play as a catalyst but as a poison to the BzH autoxidation. Such property remains even after being oxidized with concentrated nitric acid (entry 8). We speculate that this is probably due to the adsorption of benzoyl radicals by the large number of

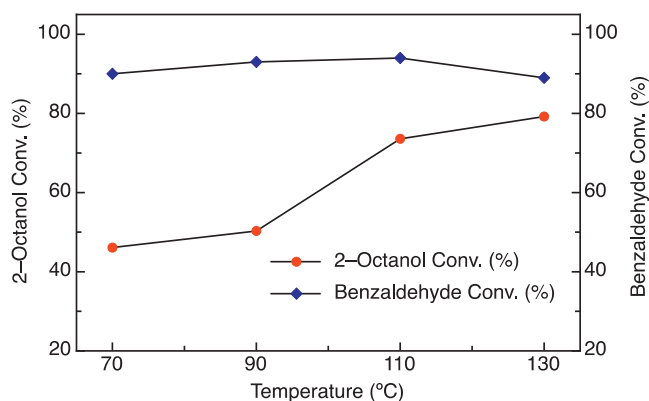


Fig. 2. The effect of temperature. General conditions: 2-octanol (10 mmol), BzH (1.25 eq.), Co/NSC (5 mg), O₂ (balloon pressure), 7 h. BzH was added portionwise over 4 h.

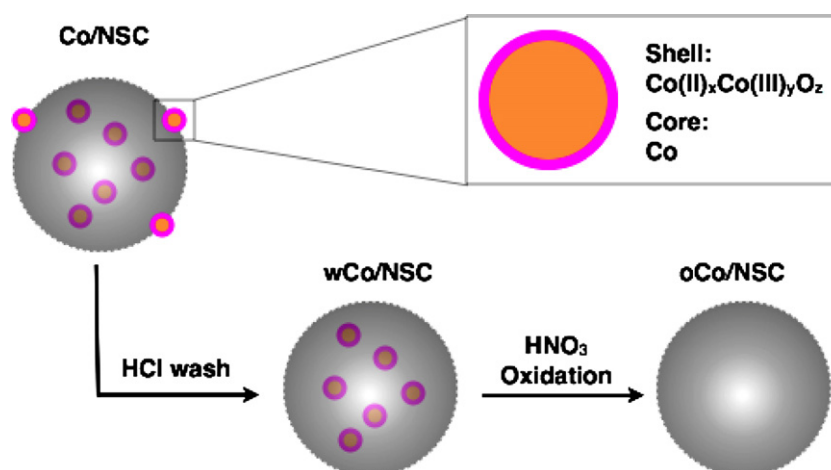


Fig. 3. Schematic illustration of structures of Co/NSC, wCo/NSC and oCo/NSC.

Table 3
Comparison of catalytic performances in the oxidation of 2-octanol.

Entry ^a	Catalyst	BzH conv. ^d (%)	2-Octanol conv. (%)	2-Octanone sel. (%)
1	–	84	30	100
2 ^{b,c}	Co/NSC	99	98	100
3 ^b	wCo/NSC	92	88	97 ^d
4 ^b	oCo/NSC	87	57	97 ^d
5 ^c	Co(II)Ac	98	96	100
6 ^c	Co(II)Pc	97	92	100
7 ^b	AC	1	0	100
8 ^b	oAC	9	1	100

^a General conditions: 2-octanol (10 mmol), BzH (20 mmol), O₂ (balloon pressure), 110 °C, 16 h; BzH was added portionwise over 4 h.

^b 5 mg of carbon catalysts were added.

^c Co contents were fixed to be 3 μmol.

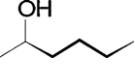
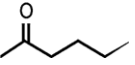
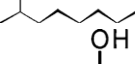
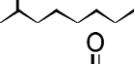
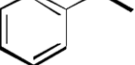
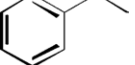
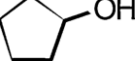
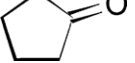


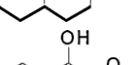
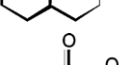
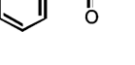
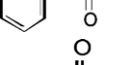
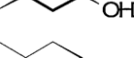
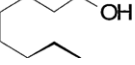
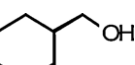
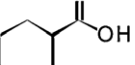
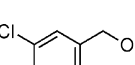
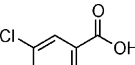
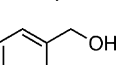
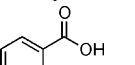
^d The main byproduct was hexyl acetate (Baeyer–Villiger oxidation product).

nanopores of AC. The nanopores generally serve as traps for benzoyl radicals, interrupting radical chain reactions.

3.4. Application scope

The system can be easily applied to various secondary alcohols, e.g., benzylic, linear aliphatic, as well as cyclic aliphatic alcohols. With the identical reaction conditions optimized for 2-octanol, almost quantitative conversions were easily obtained for a range of alcohols along with satisfactory selectivities to ketones (Table 4, entry 1–7). Notably, our system exhibited the same degree of efficiency towards both activated and non-activated alcohols, especially under solvent free conditions. This remarkable feature could be very useful for the oxidation of alcohols that are thought to be challenging for other aerobic oxidation methods. Although two equivalents of BzH are sacrificed in the reaction, the produced benzoic acid should not be considered as waste because it is one of the most largely produced chemicals in industry [20]. Benzoic acid can be easily separated from products by partitioning between alkaline aqueous solution and organic solvent. Primary alcohols were smoothly oxidized to corresponding acids (entry 8–10); however, small percentages of benzoate byproducts (<10%) were observed from the reaction of alcohols and benzoic acid (entry 8, 9). Heteroaromatic substrate containing nitrogen atom seems to be poisonous to the catalyst, e.g., 3-pyridinemethanol (entry 11), resulting in retarded aldehyde autoxidation and very low conversion of the alcohol.

Table 4
Oxidation of various alcohols.

Entry ^{a,b}	Substrate	Product	Conv. (%)	Sel. (%)
1			95	100
2			97	100
3			98	100
4			92	98 ^c
5			92	96 ^c
6			93	100
7			95	100
8			94	90
9			93	92
10			93	75 ^d
11 ^e			9	100

^a General conditions: substrate (10 mmol), BzH (20 mmol), Co/NSC (5 mg), 110 °C, 16 h, O₂ (balloon pressure); benzaldehyde was added portionwise (25%/h).

^b Over 97% of benzaldehydes were converted to benzoic acid, unless otherwise mentioned.

^c The main byproduct was the corresponding Baeyer–Villiger oxidation product.

^d The selectivity to the corresponding aldehyde was 25%.

^e The benzaldehyde conversion was 58%.

Table 5
Oxidation of 2-octanol in the presence of additives.

Entry ^a	Additive	BzH conv. (%)	2-Octanol conv. (%)
1	RuCl ₃ (1 mol%)	10	6
2 ^b	RuCl ₃ (1 mol%)	1	<1
3 ^c	RuCl ₃ (0.5 mol%)	81	32
4	TEMPO (1 mol%)	3	0

^a General conditions: 2-octanol (10 mmol), BzH (12.5 mmol), Co(OAc)₂ (1 mol%), O₂ (balloon pressure), 90 °C, 16 h; BzH was added portionwise over 4 h.

^b 10 mL of EtOAc used as solvent.

^c Co(OAc)₂ (5 mol%).

Table 6
Oxidation of 2-octanol with peroxide and peracid.

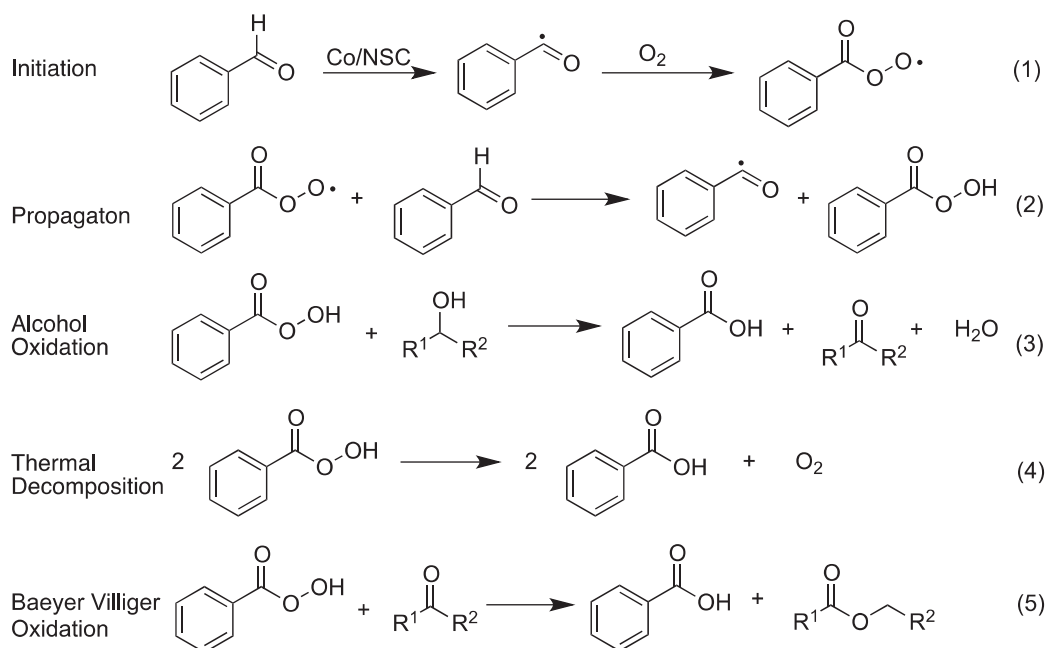
Entry ^a	Oxidant	Catalyst	2-Octanol conv. (%)	2-Octanone sel. (%)
1 ^b	Benzoyl peroxide	Co/NSC	7	100
2 ^b	Benzoyl peroxide	–	10	100
3 ^c	mCPBA	Co/NSC	13	100
4 ^c	mCPBA	–	23	72 ^d

^a General conditions: 2-octanol (10 mmol), Co/NSC (5 mg, if used), O₂ (balloon pressure), 110 °C, 6 h; after 6 h, no remains of oxidant in all entries.

^b Benzoyl peroxide (2 mmol), wetted with ca. 25% water.

^c mCPBA (4 mmol).

^d The main byproduct was hexyl acetate.



Scheme 1.

3.5. Mechanistic studies

In the reported Ru–Co system, RuCl_3 was proposed to serve as the core catalyst that forms the real oxidant, i.e., Ru(V) intermediate with peracid, which comes from the cobalt catalyzed aldehyde autoxidation [10]. So we thought whether ruthenium would play any role in our system, although our system worked very well without it. Unexpectedly, RuCl_3 behaved more like an inhibitor rather than a promotor when Ru and Co was both set to be 1 mol%, even in the solvent of ethyl acetate (Table 5, entry 1, 2). Then we adjusted the ratio of Ru:Co to 1:10 (0.5 mol% vs. 5 mol%) and the result turned to be much better (entry 3). However, the conversion of alcohol received no improvement from Ru. These results seem to be inconsistent with the reported mechanism [10], where Ru reacts only with peracid and does not intervene in the radical chain reaction. We argue that in our system, the radicalization of BzH on cobalt is a very slow process, and the formation of peracid mainly depends on the radical chain reaction, therefore it can be inferred that Ru interrupts the peracid formation by reacting with benzoyl radical. This also explains why significant

improvement was observed through adjusting Ru:Co ratio. Thus it could be generally concluded that any substance that interfere with the radical chain reaction will lead to the failure of this method. This conclusion was further evidenced by the reaction conducted in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (entry 4), which is commonly known as a radical scavenger. Another conclusion is that the Ru(V) intermediate is not a better oxidant than peroxybenzoic acid under our conditions.

To investigate more on the catalytic role of cobalt in the oxidation of alcohol, we designed two sets of reactions with meta-chloroperoxybenzoic acid (mCPBA) and benzoyl peroxide as the oxidants, in the presence/absence of Co/NSC. The common feature is that the formation of real oxidant is independent of cobalt. The results, as shown in Table 6, indicate that cobalt does not have direct effect on the alcohol oxidation step. Interestingly, cobalt seems able to suppress the Baeyer–Villiger (BV) oxidation reaction, which is considered to be a side reaction that produces ester byproduct (entry 3, 4). This also explains the trace amount of byproducts observed in entry 3 and 4 in Table 3.

The significant improvement of alcohol oxidation in the presence of Co/NSC can be rationalized by considering three competing reactions, i.e., alcohol oxidation to ketone by peracid (Scheme 1, Eq. (3)), thermal decomposition of peracid (Eq. (4)) and BV oxidation of ketone to ester (Eq. (5)). The rate of the first reaction is proportional to the temperature and peracid concentration. As the formation of radical initiator is a relatively slow process, and it can be largely accelerated in the presence of cobalt (Eq. (1)), therefore the resulted dynamic peracid concentration is increased (Eq. (2)), leading to a higher efficiency of BzH for alcohol oxidation. The thermal decomposition rate also increases with temperature. However, the increment is probably smaller that of oxidation reaction, so the net effect is still the improved alcohol oxidation performance. BV oxidation affects the product selectivity by producing ester byproduct. Since it is suppressed by cobalt, this side reaction can be ignored in most cases.

4. Conclusions

A heterogeneous cobalt based aerobic oxidation system has been successfully established. This system is equally efficient

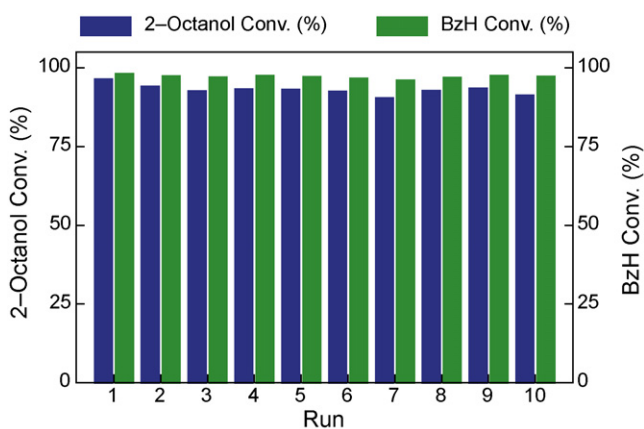


Fig. 4. Reusability test of Co/NSC in the oxidation of 2-octanol. Reaction conditions: 2-octanol (10 mmol), BzH (20 mmol), Co/NSC (5 mg), 110 °C, 16 h, O_2 (balloon pressure); BzH was added portionwise (25%/h).

towards a wide range of alcohols, e.g., benzylic alcohols, linear aliphatic alcohols, and cyclic aliphatic alcohols, etc. It also features solvent free reaction conditions, eliminated use of precious metal and reduced use of aldehyde. The preparation of Co/NSC demonstrates an easier method for the carbon supported cobalt catalyst. Moreover, the nanoshell carbon has been proved to be a good supporting material for this specific type of reaction.

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