



Cobalt oxide supported gold nanoparticles as a stable and readily-prepared precursor for the in situ generation of cobalt carbonyl like species

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ARTICLE INFO

Article history:

Received 21 July 2011

Revised 10 September 2011

Accepted 15 September 2011

Available online 21 September 2011

Keywords:

Cobalt carbonyls

Pauson–Khand reaction

Alkoxy carbonylation

Alternative catalyst

ABSTRACT

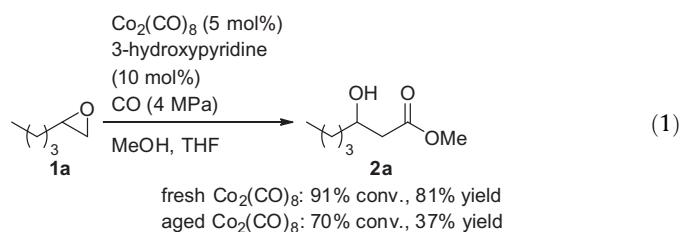
A treatment of cobalt oxide supported gold nanoparticles (Au/Co₃O₄) under syngas atmosphere effectively generated a cobalt carbonyl-like active species in the reaction vessel. The preparation of Au/Co₃O₄ was quite simple and the in situ generated cobalt species could be used as a stable and easy handling alternative for dicobalt octacarbonyl without bothersome purification prior to use. The reactions, which are sensitive to the purity of the dicobalt octacarbonyl, such as the alkoxy carbonylation of epoxides and the Pauson–Khand reaction, smoothly progressed with Au/Co₃O₄.

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Cobalt carbonyls are one of the most versatile reagents among metal carbonyls. Dicobalt octacarbonyl¹ (Co₂(CO)₈) in particular is broadly used as a catalyst for hydroformylation,² carbonylation reactions,³ and amidocarbonylation.⁴ It is also employed as a stoichiometric reagent for the Nicholas reaction⁵ and the protection of alkynes.⁶ However, Co₂(CO)₈ often requires sublimation and/or recrystallization prior to use to obtain good catalytic activity and repeatability because of decomposition during storage even below 0 °C under an inert gas atmosphere due to the dissociation of CO. Furthermore, a less obvious problem is that a preparation of Co₂(CO)₈ from Co(II) salt requires a harsh condition, for example CO/H₂ pressure of 3500 psi (ca. 24 MPa), and a temperature of 150 °C.^{7,8}

Recently, we have reported a novel function of cobalt oxide supported gold nanoparticles (Au/Co₃O₄) to provide Co₂(CO)₈-like species under a CO/H₂ atmosphere.^{9a–c} The active species were formed by the reduction of the support metal and by subsequent binding to CO. The existence of Co(0) after the treatment of Au/Co₃O₄ under H₂ was clearly observed using an XRD and a XANES spectra.^{9d} Au nanoparticles played an important role for the first reduction step to generate spillover hydrogen, therefore Co₃O₄ without Au did not show any catalytic activity for the hydroformylation of olefins.^{9a,c} Au/Co₃O₄ can be readily prepared from commercial HAuCl₄·4H₂O and Co(NO₃)₂·6H₂O even on a large scale by simple mixing of a me-

tal solution and a base solution at rt (co-precipitation method).^{9b,c} Since the obtained solid consisted of gold(0) and cobalt oxide, it was fairly stable to air and moisture at least for several months. Au/Co₃O₄ worked as a recyclable heterogeneous catalyst in nonpolar solvents such as heptane.^{9a,c} However, our initial investigations proved that this heterogeneous system showed poor activity for the alkoxy carbonylation of epoxides and the Pauson–Khand reactions (PKR). Therefore, we have attempted to use Au/Co₃O₄ as a precursor of homogeneous Co₂(CO)₈-like species by employing resolvable polar solvents. This catalyst system was able to generate fresh active species continuously during the reaction, thus it was consummately ideal for the reactions sensitive to the purity of Co₂(CO)₈.



Co₂(CO)₈ catalyzes the alkoxy carbonylation of epoxides to give β-hydroxyesters. This was first reported in 1961^{10a} and several extended works were found in recent years.^{10b–h,11} Although specific mention about sensitivity to the purity of Co₂(CO)₈ did not appear

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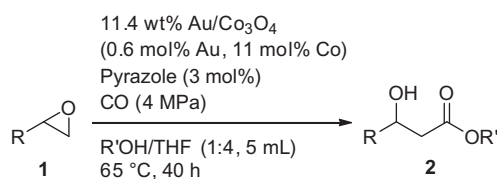
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in the literatures, this reaction seemed to be greatly dependent on the fineness of $\text{Co}_2(\text{CO})_8$. We investigated the difference of catalytic activity between a freshly sublimed $\text{Co}_2(\text{CO})_8$ and an aged one by following Jacobsen's procedure^{10d} (Eq. 1). A fresh catalyst gave the result of 91% conversion and 81% yield. On the other hand, the catalytic activity decreased to 70% conversion and 37% yield after storage for several weeks at 4 °C under a N_2 atmosphere. The result of the initial survey of the reaction conditions including solvent, additive, syngas ratio, temperature, and reaction time is shown in Table 1. Under the conditions of Table 1, entry 1, only 2% of the desired β -hydroxyester was obtained along with a large amount of nucleophilic ring opening ether products. Whereas an addition of 3-hydroxypyridine was reported in the literature to improve the reaction efficiency,^{10c} it was found to be ineffective for the $\text{Au}/\text{Co}_3\text{O}_4$ catalyst system with a negligible improvement of the product yield (Table 1, entry 2). Recently, pyrazole was also reported as an additive,^{10f} and it was employed for the reaction because it worked better than 3-hydroxypyridine (Table 1, entry 3). A low yield of the desired product was caused by the formation of several by-products including ketones, acetals, and ethers.^{10f} While hydroformylation of epoxides could take place under a CO/H_2 atmosphere,¹² β -hydroxyaldehyde or reduced 1,3-diol products were not detected in the reaction mixture. Since the most significant side reaction among them was an ether formation by a nucleophilic attack of MeOH, the amount of MeOH was restricted. As a result, the decrease in MeOH suppressed the formation of byproducts and gave a better yield of β -hydroxyesters (Table 1, entries 4 and 5). Additionally, increasing the reaction time at a milder reaction temperature (65 °C) and a higher CO partial pressure efficiently improved the results (Table 1, entries 6–8). Pretreating the catalyst prior to each reaction was important for the efficient generation of the active species. The CO/H_2 atmosphere seemed to be preferable to H_2 since the active species exist at the initial stage of the reaction which avoids the side reactions irrespective of the catalysis (Table 1, entries 1–4 vs 5–8).

Next, we turned our attention to the substrate scope of the reaction. Although a slight difference of reactivity according to the chain length was observed, alkyl epoxides were smoothly reacted to give the desired β -hydroxyesters in moderate to good yields (Table 2, entries 1–4). Styrene oxide showed a low reactivity (Table 2, entry 5). As for alcohol nucleophiles, EtOH showed a

Table 2

$\text{Au}/\text{Co}_3\text{O}_4$ catalyzed alkoxy carbonylation using various epoxides and alcohols^{a,b}



Entry	Substrate	R'OH	Product	Yield ^c (%)
1		MeOH	2b	58
2		MeOH	2c	79
3		MeOH	2d	45
4		MeOH	2e	86
5		MeOH	2f	5
6		EtOH	2g	82
7		2-PrOH	2h	33

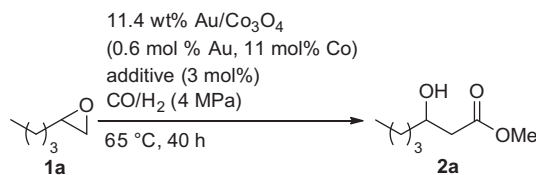
^a The catalyst was pretreated under CO/H_2 (3:1, 2 MPa) at 120 °C for 3 h in the reaction solvent prior to the reaction.

^b The reaction was conducted on a 5 mmol scale.

^c GC yield.

reactivity similar to MeOH (Table 2, entry 6). However, 2-PrOH gave a lower yield probably due to the steric problem (Table 2, entry 7).

The PKR is a formal [2+2+1] cyclization for providing cyclopentenone derivatives. Since this reaction is quite useful for constructing complex molecular skeletons, it is incorporated in many natural product syntheses.¹³ This reaction was originally reported as a stoichiometric reaction using $\text{Co}_2(\text{CO})_8$,¹⁴ and catalytic versions were developed by employing various additives¹⁵ or highly

Table 1
Optimization of reaction conditions for $\text{Au}/\text{Co}_3\text{O}_4$ catalyzed alkoxy carbonylation of epoxides

Entry	Pretreatment ^b	Additive	Solvent	$\text{CO}:\text{H}_2$	Yield ^a (%)
1 ^{c,d}	A	None	MeOH	3:1	2
2 ^{c,d}	A	3-Hydroxypyridine (10 mol%)	MeOH	3:1	3
3 ^{c,d}	A	Pyrazole	MeOH	3:1	17
4 ^{c,d}	A	Pyrazole	MeOH/THF (1:1)	3:1	26
5 ^{c,e}	B	Pyrazole	MeOH/THF (1:4)	3:1	33
6 ^e	B	Pyrazole	MeOH/THF (1:4)	3:1	48
7 ^e	B	Pyrazole	MeOH/THF (1:4)	7:1	59
8 ^e	B	Pyrazole	MeOH/THF (1:4)	CO only	68

^a GC yield.

^b Pretreatment method: (A) The catalyst was pretreated under H_2 (2 MPa) at 120 °C for 2 h in the reaction solvent prior to the reaction; (B) The catalyst was pretreated under CO/H_2 (3:1, 2 MPa) at 120 °C for 3 h in the reaction solvent prior to the reaction.

^c The reaction was carried out at 80 °C for 20 h.

^d The reaction was conducted on a 2 mmol scale in 2 mL of the solvent.

^e The reaction was conducted on a 5 mmol scale in 5 mL of the solvent.

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