

Stable and Surface-active Co Nanoparticles Formed from Cation (x) Promoted Au/x-Co₃O₄ (x = Cs) as Selective Catalyst for [2+2+1] Cyclization Reactions

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Surface-active and highly stable cobalt nanoparticles generated from alkali ion-promoted gold catalyst for catalyzed carbonylative [2+2+1] cyclization reaction, is described. The gold nanoparticle's (AuNPs) role was assumed to dissociate the CO and H₂ into atomic species on the catalyst surface by spillover, which in-situ reduces the robust mesoporous cobalt oxide to metallic cobalt ($Co^{3+} \rightarrow Co^{2+} \rightarrow Co$), as the active catalytic species that catalyzed the reaction; thereby providing up to 93% yield of cyclopentenone adducts. Prior to this, catalyst pre-treatment with H₂ gas (130 °C, 3 h, 20 atm) was performed to reduce the catalyst. It appeared that the low reducibility temperature and increased surface basicity ascribed to the presence of alkali ionpromoters in the catalyst revealed a strong correlation with the catalyst activity, for the intra- and intermolecular reactions under milder reaction conditions. Thus, a sustainable, highly reusable, and environmentally friendly green catalyst for the carbonylation reaction, such as Pauson-Khand, was developed.

Cycloaddition [2+2+1] of alkenes, alkynes in the presence of dicobalt octacarbonyl Co2(CO)8 complexes and carbon monoxide to cyclopentenones (known as Pauson-Khand reactions (PKR)) have been actively recognized and investigated for decades as an essential synthetic protocol for the preparation of cyclopentenone derivatives. The products of these reactions have found usage in several biologically active pharmaceuticals and vital natural products.^[1,2] Dicobalt octacarbonyl has been broadly used in amidocarbonylation,^[3] carbonylation,^[4] Pauson-Khand,^[5] and hydroformylation^[6] reactions. These cobalt carbonyl compounds are versatile reagents among metal carbonyls for organic and inorganic syntheses. Cobalt carbonyl complexes have been reported as homogeneous catalysts for Pauson-Khand reactions with poor catalytic performance (low product yield).^[7] Similarly, cobalt metal deposited by thermal decomposition of Co₂(CO)₈ complexes on various supports demonstrated great catalytic potential for Pauson-Khand reac-

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 Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202001841 tions of the resulting materials.^[2] Aside from the use of pure cobalt carbonyl as a homogeneous catalyst, heterobimetallic cobalt supported on ruthenium,^[8] rhodium,^[9] and charcoal^[10] has been widely reported for Pauson-Khand reactions. Muller and co-workers prepared a Raney cobalt, which acts as an active catalyst for inter- and intramolecular Pauson-Khand reaction.^[11] However, the stabilization and preparation of these cobalt carbonyl complexes require a pressure of >20 MPa and higher temperatures; this process often requires sublimation and recrystallization before use to obtain an excellent product yield and reusability due to carbon monoxide dissociation under an inert gas atmosphere during storage and below 0°C.^[12] Besides, the functional efficiency in the synthesis of these Co2(CO)8 complexes is still limited by problems of separation of the catalyst from the reaction mixture, toxicity, and volatility.^[13,14] Homogeneous cobalt carbonyl complexes are quite toxic and can precipitate during the catalytic reactions. The best possible way to overcome this, is to heterogenize the catalyst by depositing it on metal oxide supports, such as SiO₂,^[15] activated carbon,^[16] and resins.^[17,18] Incorporating these active catalytic sites on the metal oxides through chemical and physical exchanges can create a stable heterogeneous catalyst, leading to an economical and environmentally friendly "green" process chemistry.

The utilization of heterogeneous catalytic systems for carbonylation reactions such as Pauson-Khand has been a subject of intense interest in academia and chemical industries. Recently, metal nanoparticles have been quite efficient, useful and give excellent product yields for carbonylation reactions. These metal nanoparticles are gaining broad research interest in material science and chemistry because they display unusual chemical and physical properties, which are distinct from those of isolated molecule and bulk phase.^[19,20] Notably, supported gold catalysts are known for their superior catalytic performance in several homogeneous and heterogeneous reactions, such as oxidation,^[21] C-C coupling,^[22] cycloaddition,^[23] and reduction.^[24] To afford a bimetallic structure, it essential to support gold nanoparticles on selected metal oxides, even though the support's choice affects the catalyst's performance and durability. Gold nanoparticles supported on metal oxides have been reported for reactions such as alkoxy-carbonylation of epoxide and hydroformylation.^[25,26] In these reactions, the metal nanoparticles assisted in the spillover of H₂ and CO on the catalyst surface, thereby forming a cobalt carbonyl complex as the active catalytic site that catalyzed the reaction. For the intra- and intermolecular reaction reported by Hamasaki and co-workers,^[27] the dissolution of the active cobalt carbonyl species is necessary for the reaction to proceed smoothly and at a longer reaction time; the active cobalt species leached out of the catalyst into the reaction mixture, and hence, recyclability was not achieved. Given the drawbacks associated with these catalytic systems, in terms of catalyst stability and reusability, much attention has been drawn to developing suitable supports and catalysts for carbonylation reactions, such as PKR. However, the industrial applications are still undeveloped despite the successes recorded for transition metal-catalyzed synthesis of cyclopentenone products from their readily available substrates. On a sizeable economic scale, developing an active heterogeneous catalyst for these reactions is highly desirable.

Recently, we reported that alkali-promoted catalysts are carbonylation effective for reactions, such as hydroformylation.^[25] The alkali ions were used to modify and stabilize the mesoporous cobalt oxide, which minimized leaching of the active metallic Co species and improve the catalyst's overall binding properties and performance. Also, an evident correlation was found between the ion-promoted catalyst's reduction temperature and surface basicity with its catalytic performance. Before this, our group had earlier reported that dopants improve catalytic activities on mesoporous Co_3O_4 considerably.^[28] Other works of literature have published the enhanced catalytic efficiency of alkali-promoted catalysts^[29-31] due to the dopants electronic^[32] and structural^[29,31] effects on the metal oxides. As a continuous study of carbonylation reactions involving CO gas, we are interested in exploring the capability of this ion-promoted gold-cobalt based catalyst for [2+2+1] cyclization reactions. Motivated by this outcome, and hence the need to develop a more active and stable heterogeneous catalyst for carbonylative reactions, herein, we prepared mesoporous Co3O4 by the inverse micelle method,^[33] modified by doping with alkali metals (x) (where x =Cs, Li, K, Ca and Na), to act as ion-promoters and stabilizers. Subsequently, immobilization of the AuNPs on the reducible metal oxide to afford a bimetallic structure. Under these conditions, we assumed that the ion-promoted catalyst would catalyze the Pauson-Khand reactions, based on the unique structural properties and easy preparatory steps of the catalysts, which was entirely different from others reported. To the best of our knowledge, attributing catalytic performance to the concentration of basic sites and low reducibility temperature of a catalyst for Pauson-Khand reactions have not been reported. The temperature-programmed measurements were performed, and the catalytic performance of the supported catalyst was studied in detail with respect to the pre-treatment of the catalyst with hydrogen, recyclability, and parameter effects (catalyst loading, temperature, solvent, and pressure). The catalyst was applied for the inter -and intramolecular PK reactions (Scheme 1) by investigating the alkali ions and the gold nanoparticle's role in the overall catalyst. Also, the catalyst's reusability makes our catalytic system more viable and could be used as an easy handling alternative to other carbonyl catalysts, which requires a tedious purification process.



Scheme 1. (a) Intra- and (b) intermolecular PK reactions.

The cation-promoted catalysts were synthesized via the deposition-precipitation method with urea and employed as an active catalyst for inter- and intramolecular PK reactions. The reactions were carried out with excellent selectivity and yield to the desired cyclopentenone products under CO atmosphere; though more favorable for the intra PKR, with catalytic activity in order of (5 wt.%) Au/Co₃O₄ (**Xc**) < Au/Ca–Co₃O₄ (**Xd**⁴) < Au/K–Co₃O₄ (**Xd**³) < Au/Na–Co₃O₄ (**Xd**²) < Au/Li–Co₃O₄ (**Xd**¹) < Au/Cs–Co₃O₄ (**Xd**⁴). We assumed that the notable enhanced catalytic performance of the catalyst could be attributed to the cobalt nanoparticles formed on the catalyst surface by spillover H₂ from the AuNPs. The activity was also linked to the increased surface basicity of the nanomaterials.

The nanomaterial's surface basicity was evaluated by CO2-TPD measurements because of the substantial role of basicity in the carbonylation reactions involving CO $gas^{\scriptscriptstyle [25]}$ (Figure 1a and Figure S4). The significant role of ion-promoters in catalytic reactions is still unclear, despite it being mentioned in literature. We believe the alteration of the surface basicity could explain these promoter's role in the enhanced catalytic performance. Another interesting observation is the increase in catalytic activity, which correlated with the cation's charge/size ratio; this particular observation has not been reported for carbonylation reactions. Helwani et al. reported that alkali metal ions on the surface of catalysts are known to improve the nanomaterial's surface basicity due to their highly electropositive nature.^[34] In this work, the alkali metal ions caused a remarkable increase in the catalytic performance towards the Pauson-Khand reaction. Under the reaction conditions of CO (20 atm), 130 °C, and 6 h, it was observed that the Cs-promoted gold catalyst was the most active to the nonpromoted Xc catalyst and others for the oxygen-tethered cycloaddition reaction, with the highest yield of the cyclopentenone product achieved at 87.2% (Figure S5). This was ascribed to the highly electropositive nature of the Cs metal, which increased the basic site concentration in the catalyst and enhanced its catalytic efficiency for the PKR; further confirming the induced promotional effect of these cations on the catalysts (Figure 1a and Figure S4). It is important to note that incorporating the Au metal on the support matrix slightly improved the catalyst's basic strength. Therefore, basicity played a crucial role in the higher catalytic performance for the PKR. The improved catalytic strength and activity were also linked to the nanomaterial's low reduction temperatures at





Figure 1. Comparison of (a) CO₂-TPD, (b) CO-TPR and (c) H₂-TPR profiles to justify the promotional effect of the Cs⁺ on the nanomaterials.

higher $\rm H_2$ and CO consumption (Figure 1b and Figure 1c) (see Supplementary Figure S4 for more details).

The pore structure and BET surface areas were noticeably affected by the Au loadings (Table S1). Also, an increase in the Au loadings up to 25 wt.% provided a lower yield of the product (Table S3, entry 10). Although, the catalysts were crystalline in their framework structures, as observed from the acquired HR-TEM micrographs (Figure S1), as well as the well-resolved p-XRD diffraction patterns (Figure S3a). A characteristic Type IV isotherm was observed for Au catalyst and support, indicating the material's mesoporous nature (Figure S3b). It is noteworthy that the BJH pore diameter/volume and BET surface area decreased after incorporating the AuNPs on the reducible Cs–Co₃O₄ (Table S1). From the TGA spectra, the decomposition of the organic matter in 5% Au/Cs–Co₃O₄, in the temperature range of 104–800 °C, suggests the catalyst's safety when used below 104 °C (Figure S3d).

Next, we began our investigation by screening the newly developed catalyst, using the oxygen-tethered enyne prototype substrate (1 a), in order to probe the feasibility of the goldcobalt based catalysts under the reaction conditions of 130°C, 6 h and CO (20 atm) (Figure S5). Before this, catalysts pretreatment with hydrogen gas were performed (H₂ pressure 20 atm, 130 °C, and 2-3 h). Our initial experiments reveal that the more demanding pure cobalt support Co₃O₄ (Xa) showed little or no beneficial effect for the [2+2+1] cyclization reaction, and the series in the activity of the catalyst follows the order $Xc < Xd^4 < Xd^3 < Xd^2 < Xd^1 < Xd^*$. In this study, we assumed that the metallic cobalt species formed on the catalyst surface by the spillover process were shown to be the active and stable heterogeneous catalyst that catalyzed the PK reactions. Table 1 and Figure 3 lists the series of the cyclopentenone products, which have been prepared by the Xd* catalyst, promoted the [2+2+1] cyclization reaction under CO pressure in THF and other solvents. All the cyclopentenones synthesized in this work are in oily form and high boiling, which were readily purified by flash column chromatography using ethyl acetate, hexane, dichloromethane as eluents at different times. For the optimization of reaction conditions, the cyclization of the envne (1 a) by Xd* in THF and other solvents were attempted (Table 1, entries 1-4). The THF gave the best yield

Table 1. Effect of reaction conditions using 5% Au/Cs–Co ₃ O ₄ (Xd*). ^[a]							
Entry	Solvents	Cat. Xd *[g]	<i>T</i> [°C]	Press. [atm]	Conv. [%] ^[b]	Sel. [%] ^[b]	Yield [%] ^[b]
1	THF	0.3	130	20	96.5	90.4	87.2
2	DMF	0.3	130	20	93.1	55.8	51.9
3	Toluene	0.3	130	20	62.7	24.3	15.4
4	Dioxane	0.3	130	20	81.9	68.3	55.7
5	THF	0.8*	130	20	98.2	95.6	93.8*
6	THF	0.1	130	20	83.3	77.1	64.9
7	THF	0.8	110	20	79.8	68.6	54.6
8	THF	0.8	90	20	36.2	51.4	18.5
9	THF	0.8	150	20	98.5	90.2	88.9
10	THF	0.8	130	10	67.9	54.6	37.2
11	THF	0.8	130	5	51.3	18.9	9.6
12 ^[c]	THF	0.8	130	20	99.8	31.3	30.9
13 ^[d]	THF	0.8	110	20	60.2	49.3	29.5
14 ^[e]	THF	0.8	110	20	81.2	25.3	20.4

[a] Reaction conditions: Enyne **1a** (0.3 mmol) and 6 h reaction time. Before reaction, the catalyst (**Xd***) was preheated with H₂ gas (130 °C, 20 atm, 2–3 h) in 12 mL THF. [b] Selectivity, conversion, and yield (%). [c] 20 h, **1a** (0.3 mmol), THF (12 mL), **Xd*** (0.8 g), CO (20 atm) and temp. (130 °C). [d] No H₂ pre-treatment (110 °C, 20 atm, 6 h). [e] No H₂ pre-treatment (110 °C, 20 atm, 12 h).

among the solvents screened in this study; presumably due to its role in stabilizing the active Co species formed on the catalyst surface and attributed to its cyclic ether functionality and moderate polarity in its ability to dissolve a wide range of compounds (Table 1, entry 1). Next, we varied the catalyst loadings to see its effect on the cyclization reaction. Increasing the catalyst amount from 0.3 to 0.8 g gave a better yield of the product at 87.2% and 93.8%, respectively, compared to when the amount was reduced to 0.1 g (64.9%) (Table 1, entry 6). It is noteworthy that reactions conducted below 130°C gave slightly lower conversions and yields of the isolated product (Table 1, entry 7 and 8). At higher temperatures up to 150°C (Table 1, entry 9), only a slight decrease in the product yield was observed after 6 h reaction time, with the substrate almost consumed when the reaction time was increased to 20 h (Table 1, entry 12). While some reactions will proceed with better yields, we explored other milder reaction conditions, such as reduced CO pressure, which might tolerate the enyne substrate's functionality and sensitivity. To our surprise, ex-



tremely poor substrate conversion and product yield was obtained at 51.3% and 9.6%, respectively (Table 1, entry 11).

With the preferred reaction conditions in hand, we sought to explore the catalyst versatility on this PKR protocol and to establish an extensive understanding of the substrate structures on reactivity, utilizing various substrates with varying degree of functionality (Figure 2). First, we investigated the feasibility of cyclizing the as-synthesized oxygen-tethered enynes 1a-1g under the optimized reaction conditions of 130°C, 6 h, and 20 atm (Figure 3a). To our delight, the cyclopentenones 2a-2e produced were of excellent yields. An attempt to synthesize enones with N-heteroatoms were unsuccessful, and instead, gave a trace amount of the product 2g, which were rather unidentifiable. Likewise, a trace amount of the 2f was recovered from the reaction mixture with the sterically congested alkyl ortho-substituted enyne 1 f. For the intermolecular PKR, cyclization of the substrates 1h-1p proceeded to moderate and higher yields of the products 2h-2p in the range of 43.2-80.9% (Figure 3b). Interestingly, increasing the alkene's carbon chain length on the 1i substrate, provided a much better yield of 2i (75.8%), compared to the alkene substrate 1h with shorter chain length, which recorded a yield of 70.3% (2h). A similar trend was also observed for 2j and 2k, though, with a more improved product yield at 77.5% and 80.9%, respectively; presumably due to the single triple bonds attached to alkyne in the 1j and 1k substrates, compared to 1i and 1h with double triple bonds in their molecules. Notably, steric hindrance also influenced the **21** and **2m** yields, due to the phenyl and methyl substituents attached to the **11** and **1m** alkene moieties. Hydroxyl containing terminal alkynes in the **1n–1p** substrates were attempted, and the **2n–2p** product yields were also affected by the substituents attached to their individual alkyne moieties, apparently due to the steric effect.

To further elucidate the active sites on Xd*, its catalytic efficiency was investigated after hydrogen pre-treatment (130°C, 2 h, 20 atm). Under the same reaction conditions (110°C, 20 atm), appreciable improvement in the cyclopentenone yield was observed at 54.6% after 6 h (pre-treated with H₂) (Table 1, entry 7), and decreased significantly to 29.5% (6 h) and 20.4% (12 h) without H₂ pre-treatment (Table 1, entry 13 and 14). The XRD of the pre-treated Xd* catalyst (spent) shows the absence of Co₃O₄ peaks and the formation of metallic Co species that catalyzed the [2+2+1] cyclization reaction (Figure. 4c). As shown in Figure 4a and 4b, it was established that the active species was not Co₂(CO)₈ or HCo(CO)₄ usually formed from leaching that catalyzed the PKR, but the metallic Co generated on the catalyst's surface. In practice, heterogeneous catalytic systems are known to suffer severe leaching of their active sites during reactions and eventually lose its catalytic performance. Although the maximum reusability was not tested in our system, but from our observation, no significant leaching of the active sites was observed. Figure. 4a shows that the product yield in the 1st cycle was still much higher than the fresh catalyst, with a notable increase observed in the 6th cycle,







Figure 3. (a) Intra- and (b) intermolecular PK reactions. Reaction conditions: Catalyst **Xd*** (0.8 g), substrates (0.3 mmol), CO (20 atm), temp. (130 °C), THF (12 mL) and 6 h reaction time. The catalyst was pre-treated under the conditions of 130 °C, 20 atm (H₂) and 2–3 h, before the experiments.

indicating its stability. The insignificant decrease observed in the last two cycles could be due to the catalyst's slight deactivation arising from the product's contamination. As shown in Figure 4b, the promotional effect of the alkali-ions on the catalyst was also evident in the reusability of **Xd*** and its nonpromoted counterpart (**Xc**), indicating that the Cs metal, assisted in stabilizing the active Co species in the catalyst, hence the insignificant leaching observed.

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The heterogeneity test on Xd^* was conducted for the [2+2]+1] cyclization reaction to determine if the active Co species leached into the reaction mixture. Firstly, we ran the reaction at the standard time; after that, the nanocomposite catalyst was filtered off, and the filtrate was returned into the autoclave reactor for 3 h, with stirring speed maintained at 450 rpm, under the optimized reaction conditions: 130°C, 20 atm. Interestingly, no significant change in the conversion was observed after 3 h reaction time, based on the GC-FID results obtained (Figure. S7), indicating no possible bleeding of the active metallic Co species into the solution. Although, the elemental analysis by ICP-OES reveals < 1.3 mg/L of the metallic Co species was leached into the reaction mixture. We can infer from the hot filtration test that there was a strong interaction between the AuNPs, Cs-promoter, and the robust mesoporous cobalt oxide support. The formation of this active metallic cobalt species that catalyzed the intra- and intermolecular PKR was also evident from the immediate FT-IR analysis of the spent nanocomposite catalyst (Figure. S8). Prior to this, the nanocomposite catalyst was re-activated by drying in a vacuum oven at 70°C for 1 hr. From the FT-IR spectra of the spent catalyst, the M-Co metal bands due to 551 and 653 cm⁻¹ appeared in the spectra. No peak assigned to Co₂(CO)₈ and HCo(CO)₄ species at 2050 and 2030 cm⁻¹, respectively, were seen.^[35] This further confirms the absence of CO-bond species or non-adsorptions of the carbonyl vibrational bands in the catalyst's spectra, indicating that the cobalt carbonyl complex was not responsible for the PKR, but rather the active solid Co metal formed on the catalyst surface. Interestingly, no trace amount of the cobalt carbonyl species was observed in the NMR spectra analysis, indicating an effective procedure in the catalyst separation and product isolation.



Figure 4. (a) Reusability studies of 5 % Au/Cs–Co₃O₄ and (b) Comparison between 5 % Au/Cs–Co₃O₄ (**Xd***) and 5 % Au/Co₃O₄ (**Xc**) catalysts, in their 1st and 6th run. The reusability test was carried out using the as-synthesized oxygen-tethered enyne substrate (**1a**), with the optimized reaction conditions: 130 °C, 6 h, THF (12 mL), 0.80 g (**Xd***), and 20 atm (CO). The catalyst was pre-treated with H₂ gas (130 °C, 2–3 h, 20 atm) before the 1st run; for subsequent runs, the hydrogen pre-treatment was not repeated. (c) p-XRD of the fresh (before H₂ pre-treatment) and spent (after H₂ pre-treatment in 12 mL THF, 130 °C, 20 atm, 2 h) 5 % Au/Cs–Co₃O₄ catalyst.



The effect of H₂ and CO gas in the catalyst's reducibility suggests that it improves the reduction behavior of Co₃O₄.^[26,36] In this work, the gold nanoparticle's role was believed to cause a spillover effect of the H₂ and CO gas on the catalyst surface. The H₂ gas, been more reducing (Figure 1c), reduces the mesoporous Co_3O_4 to Co; the formed active Co species transformed a variety as-synthesized oxygen-tethered 1, 6 enynes to bicyclic cyclopentenones with excellent yields. It is essential to note that Co metal was mainly responsible for the PK reaction. The AuNPs neither promoted the catalytic activity by synergy with the metallic cobalt nor interfered with the cyclization reaction over the cobalt metal. Also, we attributed the superior performance of this alkali-promoted catalyst (5% Au/Cs-Co₃O₄) in the cyclization reaction with carbon monoxide, to the combined effects of the catalyst structure, increased surface basicity, and low reduction temperatures. It's noteworthy that the alkali cations promoted and induced the robust Co₃O₄ and catalyst stability, which minimized leaching of the active Co species. Another more extensive feature of this catalytic system is the reusability, in which the catalyst was stable after many cycles, as well as the steady supply of the active Co species during the reaction. Therefore, we concluded that the experimental simplicity and catalyst reusability are incredibly attractive and could be useful in academia and chemical industries as a stable and easy handling alternative to the homogeneous catalytic systems.

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Conflict of Interest

The authors declare no conflict of interest.

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