

Cobalt Nanoparticles on Charcoal: A Versatile Catalyst in the Pauson–Khand Reaction, Hydrogenation, and the Reductive Pauson–Khand Reaction

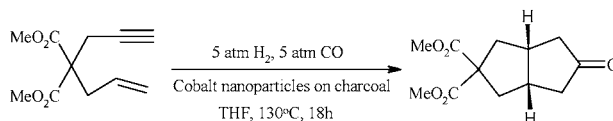
Seung Uk Son, Kang Hyun Park, and Young Keun Chung*

School of Chemistry and Center for Molecular Catalysis, Seoul National University,
Seoul 151-747, Korea

ykchung@plaza.snu.ac.kr

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ABSTRACT



Dispersions of nanometer-sized cobalt particles with very high stability were prepared in charcoal and analyzed by electron microscopy and X-ray analysis. The resulting *cobalt nanoparticles on charcoal* (CNC) were successfully used as a catalyst for the carbonylative cycloaddition of alkyne, alkene, and carbon monoxide (Pauson–Khand reaction), hydrogenation, and the reductive Pauson–Khand reaction.

The preparation and characterization of metal nanoparticles is currently of considerable practical and theoretical interest because such materials fall into an intermediate state of matter between the molecular and the bulk and frequently display unusual physical and chemical properties.¹ For noble metal colloids, catalytic applications are considered,² since a unique combination of reactivity, stability, and selectivity is expected. During the past decade, transition metal colloids were revealed as very efficient catalysts for various reactions, such as hydrogenation,³ oxidation,⁴ hydrosilylation,⁵ coupling reaction (Heck reaction and Suzuki reaction),⁶ and some photocatalytic reactions.⁷ Recently, we reported⁸ the catalytic use of colloidal cobalt nanoparticles for the Pauson–Khand

reactions. Although they are quite effective, they suffer from relatively lower stability and are more inconvenient to use than conventional heterogeneous catalysts such as Co on charcoal and Co on silica.⁹ To overcome the disadvantages of nanoparticles in catalysis, we researched how to combine the merits of conventional heterogeneous catalysts with the

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high catalytic activity of cobalt nanoparticles. We chose charcoal as a support and prepared cobalt nanoparticles on charcoal (CNC). Herein we report the first synthesis and characterization of CNC, the CNC-catalyzed Pauson–Khand reaction and hydrogenation, and the first use of CNC as a bifunctional catalyst in a sequential reaction of the Pauson–Khand reaction and hydrogenation in a one-pot reaction.

Synthesis of Cobalt Nanoparticles on Charcoal (CNC). Surfactant-stabilized nanoparticles of cobalt were prepared by the thermal reduction of dicobalt octacarbonyl.¹⁰ A transmission electron microscopic (TEM) image¹¹ confirms that the particles are well separated and that they are nearly monodisperse, having a mean diameter of 12 nm. Refluxing the synthesized cobalt nanoparticles with dried charcoal yielded cobalt nanoparticles on charcoal (CNC). A characterization of CNC was carried out by using XRD and HRTEM. The HRTEM study¹¹ shows that the mean size of nanoparticles is 12 nm, ranging from 7 to 18 nm. The crystal packing of CNC is an epsilon mode.¹² CNC is quite stable even in air for several months.

Comparative Study of Cobalt Species in the Pauson–Khand Reaction. First, we examined the Pauson–Khand reaction using CNC and other Co catalysts (Table 1).

Table 1. Pauson–Khand Reactions with CNC and Other Cobalt Catalysts^a

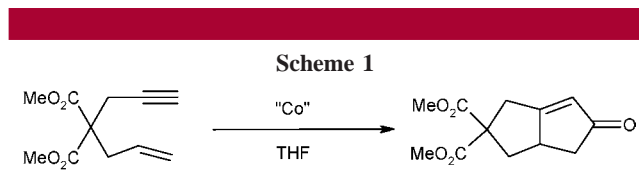
entry	catalyst	CO (atm)	yield (%) ^b
1	Co ₂ (CO) ₈ c	5	79
2	colloidal cobalt nanoparticles ^d	5	97
3	Co/C ^d	5	nr
4	CNC	1	0
5	CNC	3	25
6	CNC	5	98
7 ^e	CNC	5	62
8	recovered form #6	5	95
9	recovered form #8	5	96
10	recovered form #9	5	98
11	recovered form #10	5	98

^a Reaction conditions: CNC (0.1 g, 12 wt %), enyne (0.48 mmol), 130 °C, 18 h. ^b Isolated yield. ^c Amount used = 0.10 mmol. ^d Amount of cobalt used = 12 mg. ^e Temperature = 120 °C.

The comparison of different Co catalysts revealed considerably different reactivities. No reaction was observed with cobalt on charcoal under 5 atm of CO. Thus, high pressures were necessary with cobalt on charcoal. Under 5 atm of CO with Co₂(CO)₈, a high yield (79%) was observed. Under the same conditions, cobalt nanoparticles also gave product in an almost quantitative yield (97%). When the same Pauson–Khand reaction was carried out using CNC as a catalyst, 98% of the product was isolated. Thus, immobilization of

cobalt nanoparticles did not retard the catalytic activity of cobalt nanoparticles.

Study on the Use of CNC as Catalyst in the Pauson–Khand Reaction. Using CNC as a catalyst, we investigated the intramolecular Pauson–Khand reaction as a test reaction (Scheme 1 and Table 1).



As Table 1 shows, the optimum conditions were 5 atm of CO at 130 °C. When either the reaction temperature was decreased to 120 °C or the CO pressure was lowered, the catalytic activity was found to decrease significantly (entries 5 and 7). Thus, to preserve a high catalytic activity, the reaction temperature and CO pressure have to be maintained at a minimum of 130 °C and 5 atm of CO.

To check the recyclability, CNC was separated and reused several times. The results shown in Table 1 confirm that the catalyst maintained its high activity even after being recycled five times.

Table 2. Pauson–Khand Reaction with Various Substrates^a

entry	substrates	products	CO (atm)	yield (%) ^b
1			5	98
2			5	97
3			5	96
4			10	87
5			10	77
6			10	94
7			15	99
8			15	98

^a Reaction conditions: CNC (0.1 g, 12 wt %), 0.48 mmol of enyne, THF, 130 °C, 18 h. ^b Isolated yield.

To demonstrate the versatility of CNC, we screened various substrates for the Pauson–Khand reaction and the results are shown in Table 2. While the normal intramolecular

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Pauson–Khand reactions proceeded smoothly under 5 atm of CO (entries 1–3), internal enyne (entry 4) and heteroatom-bridged enynes (entries 5 and 6) required a higher CO pressure of 10 atm. **CNC** is also effective for intermolecular Pauson–Khand reaction (entries 7 and 8) under 15 atm of CO. When the same reactions (entries 7 and 8) were carried out using cobalt nanoparticles as catalysts, the pressure of CO was 10 atm. Thus, the catalytic activity of **CNC** is slightly lower than that of the colloidal cobalt nanoparticles for the intermolecular Pauson–Khand reaction.

Cobalt Nanoparticles on Charcoal as a Hydrogenation Catalyst. Complexes of cobalt are known to be hydrogenation catalysts but are mostly selective for conjugated systems.¹³ $\text{Co}_2(\text{CO})_8$ and derivatives are known as hydrogenation catalysts for alkenes under specific conditions, although they are decomposed to metal under a pure H_2 atmosphere.

In the previous section, we have demonstrated that **CNC** is a quite effective catalyst for carbonylative cycloaddition reaction. This result suggests that treatment of **CNC** with carbon monoxide leads to in situ generation of cobalt carbonyl species or adsorption of carbon monoxide on the surface of **CNC**. Thus, we envision that **CNC** can be used as a catalyst for hydrogenation of alkene and other related compounds as $\text{Co}_2(\text{CO})_8$ does.

We examined various substrates for hydrogenation reactions, and the results are shown in Table 3. **CNC** is an

Table 3. Hydrogenation of Olefins with Various Functional Groups^a

entry	substrates	products	temp (°C)	yield (%) ^b
1			130	90
2			130 100 80 50	98 89 n.r. n.r.
3			130 100 80 60	95 95 93 n.r.
4			100 80 60	98 98 75

^a Reaction conditions: **CNC** (0.1 g, 12 wt %), 0.48 mmol of substrate, THF, 130 °C, 18 h, 5 atm of H_2 . ^b Isolated yield.

effective catalyst for the hydrogenation of α,β -unsaturated enone, dimethyl itaconate, imine, and olefin. As expected, carbon–carbon and carbon–nitrogen double bonds were hydrogenated over carbonyl groups.¹⁵ The reaction temperature was slightly dependent upon the substrate itself: 130 °C for α,β -unsaturated enone, 100 °C for dimethyl itaconate,

80 °C for *N*-benzylideneaniline, and >60 °C for cyclopentadiene dimer. **CNC** is not effective for the hydrogenation of acetophenone and the debenzoylation of benzylphenyl ether. The hydrogenation of α,β -unsaturated enone by **CNC** implies the possibility of **CNC** as a bifunctional catalyst in sequential reactions of the Pauson–Khand reaction and hydrogenation. With these observations, we studied the use of **CNC** as bifunctional catalysts in the sequential carbonylative cycloaddition and hydrogenation of enyne or alkyne and alkene in one pot. Although the sequential reaction of Pauson–Khand reaction and hydrogenation is a useful methodology to the synthesis of natural products,¹⁶ the known reductive Pauson–Khand reactions use stoichiometric or substoichiometric amounts of cobalt complexes.¹⁷

Cobalt Nanoparticles on Charcoal as Bifunctional Catalysts: The Reductive Pauson–Khand Reaction in One Pot. Recently, the use of one particular catalyst in a tandem reaction or successive reaction has attracted much attention due to experimental simplicity and economical factors. Multifunctional catalysis involves a combination of two or more reactions requiring different types of catalytic sites. Recently, the use of the bifunctional or multifunctional catalysts has been reported in the synthesis of complex organic molecules.¹⁸

To use **CNC** as a bifunctional catalysts in the Pauson–Khand reaction and hydrogenation in a one-pot, tandem reaction, **CNC** had to satisfy the following conditions: first, carbon monoxide or hydrogen should not interfere with the catalytic activity of **CNC** for each reaction, and second, hydrogenation of substrates should not take place before a Pauson–Khand reaction of the substrate occurs. We first tested the catalytic activity of **CNC** for the hydrogenation of a Pauson–Khand reaction product (Table 4). When the

Table 4. Hydrogenation of Enones under Various Condition^a

entry	catalyst	temp (°C)	CO pressure (atm)	H_2 pressure (atm)	time (h) ^a	yield (%) ^b
1	CNC	130		1	18	
2	CNC	130		5	18	90 ^c
3	CNC	130	5	5	18	88 ^d
4	CNC	130	10	5	18	93
5	CNC	130	20	5	18	95

^a Reaction conditions: **CNC** (0.1 g, 12 wt %), 0.48 mmol of substrate, THF, 130 °C, 18 h. ^b Isolated yield. ^c Reactant (4 mol %) was recovered. ^d Reactant (3 mol %) was recovered.

pressure of hydrogen was 1 atm, no hydrogenation was observed. However, under 5 atm of H_2 , 90% of the hydrogenated product was obtained with 4% recovery of the reactant. Interestingly, the presence of carbon monoxide did not interfere with the hydrogenation.

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Table 5. Sequential Pauson–Khand Reaction and Hydrogenation^a

entry	substrates	products	yield(%) ^b
1			98 - ^c
2			90
3			95
4			94
5			92
6			87
7			54 ^d
8			43 ^d

^a Reaction conditions: CNC (0.1 g, 12 wt %), 0.48 mmol of substrate, THF, 130 °C, 18 h. ^b Isolated yield. ^c Co/C was used. ^d A hydrofomylated compound was obtained as a minor product.

Contrary to our expectation, as the pressure of CO increases, the yield becomes higher. Thus, when the pressures of H₂ and CO were 5 atm and greater than 10 atm, respectively, the yield was greater than 93%. After much experimentation, the optimum reaction conditions for the sequential Pauson–Khand reaction and hydrogenation were established: 130 °C under 5 atm of CO and 5 atm of H₂ for 18 h. We screened various substrates for the sequential

Pauson–Khand reaction and hydrogenation in a one-pot reaction (Table 5). Under our reaction conditions, no hydrogenation of enyne substrates (entries 1–6) was observed before the Pauson–Khand reaction occurred. This sequential reaction provides a straightforward approach to the bicyclic and tricyclic ketone frames from enynes. The structure in entry 2 was previously prepared by reductive Pauson–Khand cyclization.¹⁸ The structures in entries 4 and 5 in Table 5 appear as core skeletons in many natural syntheses such as those of the linear and angularly fused triquinane sesquiterpenes. Thus, CNC is a quite effective catalyst in the reductive Pauson–Khand reaction.

We have demonstrated that CNC has quite a high activity in Pauson–Khand reactions and can be used as a bifunctional catalyst in the Pauson–Khand reaction and hydrogenation in a one-pot reaction. CNC is easily recovered and reused many times without losing catalytic activity and is quite stable even in the air for several months. The use of CNC can be extended to other catalytic systems, and further work in this direction is in progress.

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Supporting Information Available: Experimental details and characterization of compounds entries 5 and 6 in Table 6 and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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