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PAPER
Qingzhu Zhang et al.
Catalytic mechanism of C–F bond cleavage: insights from QM/MM analysis of fluoroacetate dehalogenase

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Recyclable Cobalt(0) Nanoparticle Catalysts for Hydrogenations

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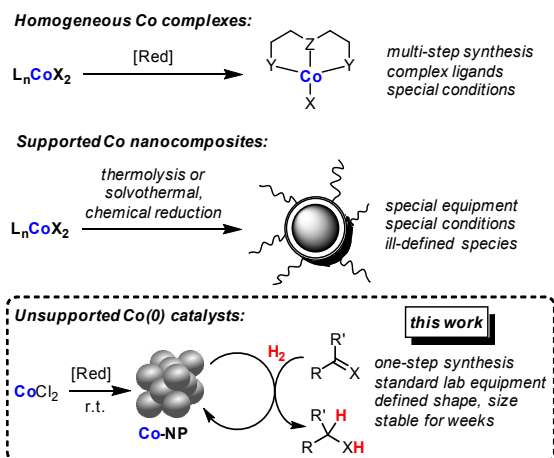
The search for new hydrogenation catalysts that replace noble metals is largely driven by sustainability concerns and the distinct mechanistic features of 3d transition metals. Several combinations of cobalt precursors and specific ligands in the presence of reductants or under high-thermal conditions were reported to provide active hydrogenation catalysts. This study reports a new method of preparation of small, monodisperse Co(0) nanoparticles (3-4 nm) from the reduction of commercial $CoCl_2$ in the absence of ligands or surfactants. High catalytic activity was observed in hydrogenations of alkenes, alkynes, imines, and heteroarenes (2-20 bar H_2). The magnetic properties enabled catalyst separation and multiple recyclings.

Introduction

The recent advent of powerful synthetic and spectroscopic techniques for the preparation and analysis of sensitive metallic compounds has prompted a rapidly increasing interest in colloidal and nanoparticulate base metal(0) catalysts.[1] The characteristics of metallic nanoparticles as hybrids between homogeneous and heterogeneous species address the key criteria for catalytic applications: high dispersion, large surface area, good separability, rich surface coordination chemistry, and high reactivity.[2] Molecular cobalt catalysts have recently been intensively studied toward their application to hydrogenation reactions (Scheme 1, top).[3,4] The complementary use of cobalt nanoparticles would be an attractive alternative to explore, but liquid-phase nanoparticle synthesis is often limited by their sensitivity, agglomeration, rapid ageing, and the availability of convenient precursor

molecules. Low-valent organometallic precursors (e.g. carbonyl, alkyl, aryl complexes) can be volatile and toxic or require multi-step syntheses, special conditions, and elaborate handling procedures (Scheme 1, center).[5] Typically, tailor-made surfactants (e.g. amines, thiols, polydentate ligands, ionic liquids) are needed to control particle size and growth and prevent agglomeration.[6]

Several heterogeneous hydrogenation catalysts were prepared by the reduction of 3d transition metal precursors with organometallic or hydride reagents and by thermal decomposition of transition metal-ligand complexes, often in the presence of stable support materials.[7] Beller and co-workers successfully applied cobalt oxide nanoparticles supported on Al_2O_3 to catalytic hydrogenations of heteroarenes, nitriles, and ketones.[8] The same group recently reported graphitic shell encapsulated Co nanoparticles for the synthesis of amines by reductive amination,[9] while Yuan reported nanocomposite Co/CoO on graphene for catalytic nitroarene hydrogenations.[10] Reusable Co nanoparticle catalysts on silicon carbon nitride were prepared by Kempe and co-workers.[11] Zhang et al.

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Scheme 1 Molecular and heterogeneous cobalt catalysts for hydrogenations.

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developed Z-selective semi-hydrogenations of alkynes with an ill-defined Co catalyst formed from cobalt(II) acetate and NaBH₄.[12] Similar chemoselectivity was reported for Co@N-graphite nanoparticles.[13]

Here, we present a complementary synthesis of a "quasi-naked" Co nanoparticle catalyst that avoids complex ligands for controlling nucleation and agglomeration (i.e. only solvent available), high-temperature conditions for crystallization, and special support materials for deposition. Very small and monodisperse Co(0) nanoparticles are accessible by the precise control of the reducing conditions in the presence of an alkali metal/arene couple (Scheme 1, bottom).[14] The resultant Co(0) catalysts present tangible advances over the current state-of-the-art in that they are easily accessible from commercial reagents, exhibit long-term stability and activity, exhibit a wide substrate scope in hydrogenation reactions, and allow facile separation and catalyst recycling. The complementary properties of such Co nanoparticles and related molecular catalysts prepared under similar conditions demonstrate the close conceptual relationship between homogeneous and heterogeneous catalysts.[4,16]

Results and Discussion

Highly pure M(0) nanoparticles (M = Mo, W, Re, Fe, Zn, Ti, Gd, U) with diameters of ≤10 nm were prepared by the reduction of metal halides with alkaline metal naphthalenides.[17] However, the related quasi-naked Co(0) nanoparticles were still elusive due to their strong superparamagnetism and the resulting agglomeration. A modified procedure has now enabled the facile preparation of small and uniform nanoparticles in quantitative yield by reduction of CoCl₂ with lithium naphthalenide ([LiNaph]) at 20 °C and centrifugation (Co-NP) or magnetic separation (mCo-NP, Figure 1a). Alkaline metal naphthalenides were also used to obtain so-called activated Rieke metals,[17x] which, however, are barely characterized and typically represent bulk metals. Nanoparticles made via the Rieke approach often show significant agglomeration and oxide impurities.[17xx] The here shown Co nanoparticles nevertheless may also support understanding of mechanism of activated Rieke metals.

Here, Co(0) formation was apparent from the immediate color change to black (Figure 1b). Use of an excessively strong reductant (E^0([NaNaph]) = −3.1 V vs. Fc/Fc⁺, cf. E^0(Co²⁺/Co⁰) = −0.28 V vs. NHE)[20] ensured high oversaturation and thus enabled excellent control of nucleation and particle growth (LaMer model).[21] The precipitates were separated by centrifugation (20,000 rpm) to obtain powderous Co(0) samples with quasi-naked surfaces. The nanoparticles could be redispersed in THF or toluene. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) displayed uniform, non-agglomerated nanoparticles of 3.4±0.4 nm diameter (Figure 1c and inset).

HAADF-STEM images showed highly ordered lattice fringes that indicate the presence and crystallinity of the Co(0) nanoparticles. The lattice distance (2.0 Å) matches that of

cubic bulk-Co⁰ (d(111) = 2.0 Å). Dynamic light scattering (DLS) documented the size distribution of the as-prepared Co-NPs in THF suspension with a mean hydrodynamic diameter of 3.6±0.9 nm (Figure 1d). Fourier transform infrared spectroscopy (FT-IR) show very weak C–H and C–O vibrations related to surface-adhered THF (Figure 1e), which documented the presence of quasi-naked nanoparticles.[17] All in all, such small size and low agglomeration in absence of specific strong binding ligands is an advancement in regard of non-blocked catalytically active surfaces and even more remarkable for nanoparticles showing attractive magnetic properties.

X-ray powder diffraction (XRD) confirmed the presence of high-purity Co and the absence of any oxide impurities (Figure S3). Glass capillaries containing the
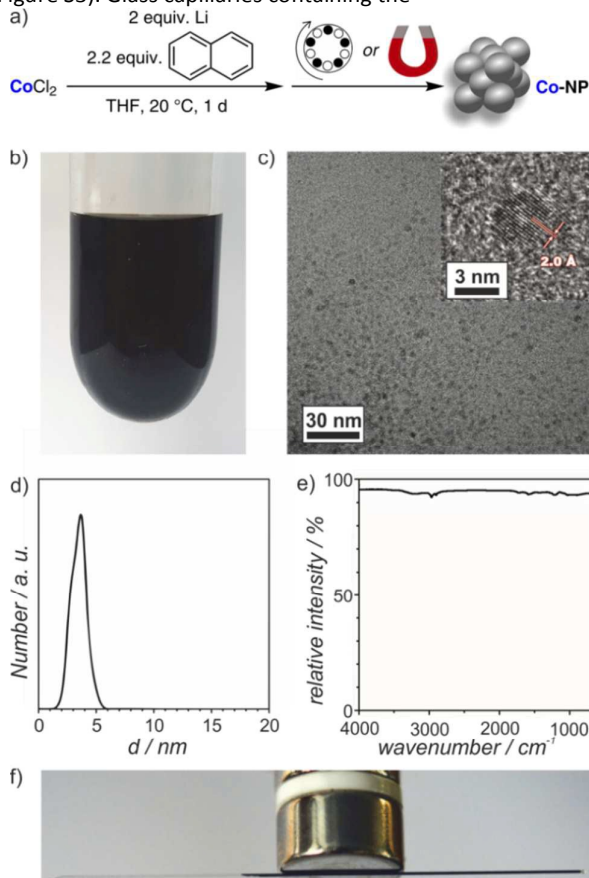

Figure 1 a) Synthesis of defined Co(0) nanoparticles (Co-NP) by reduction of CoCl2 with LiNaph and centrifugation or magnetic separation. b) Co-NP suspension in THF. c) HRTEM overview and HAADF-STEM images (with lattice fringes and lattice distance). d) Particle size distribution from DLS. e) FT-IR spectrum with weak vibrations. f) Magnetic Co-NP powder in 0.3 mm glass capillary.

powderous Co-NPs were strongly attracted to a permanent magnet (Figure 1f). The latter property was exploited in the development of a highly practical and operationally simple procedure of preparation and work-up. The quasi-naked Co-NPs were successfully isolated from the suspension by magnetic immobilization (cylindrical neodymium magnet, 10x20 mm, N45, 15 min, 4 mmol Co in 20 mL THF) instead of the centrifugation.[14,15]

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We have evaluated the catalytic activity of the freshly prepared Co(0) nanoparticles in hydrogenations of unsaturated substrates that lie outside the well-explored scope of highly polar carbonyl, nitro, and cyano compounds. There are much fewer reports of Co-catalyzed hydrogenations of non-polar or less polar substrates such as alkenes, alkynes, and imines.[22] Highly reproducible catalyst activities, facile handling, and dosing were achieved by ultra-sonication of the catalyst suspension for 1 h prior to use. Mono- and di-substituted alkenes and terminal and internal alkynes were cleanly hydrogenated under very mild conditions (1 mol% Co-NP or mCo-NP, 2 bar H_2, 20°C, 3 h). Sterically demanding,

1-5 mol% Co-NP, 2 bar H_2, THF, 20°C, 3-24 h[14]

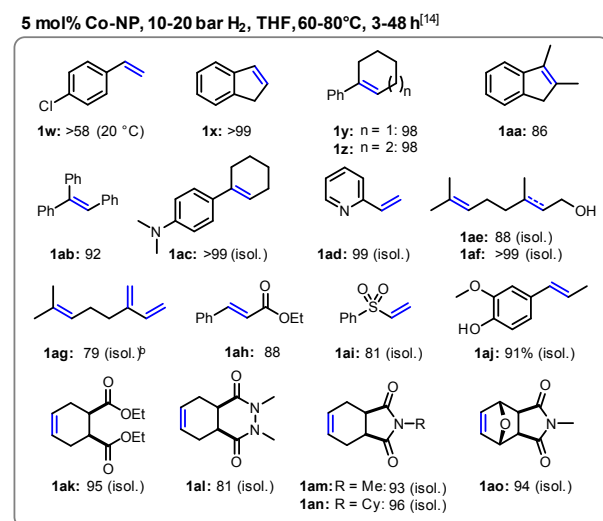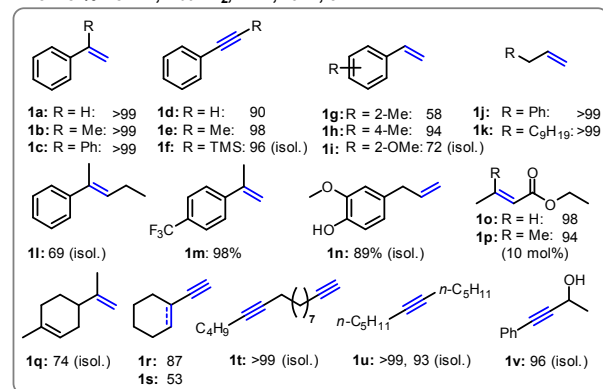**5 mol% Co-NP, 10-20 bar H_2, THF, 60-80°C, 3-48 h[14]**

Figure 2 Co-catalyzed hydrogenation of alkenes and alkynes. Blue bonds indicate the sites of π-bond hydrogenation. Standard conditions: 0.25 mmol substrate, 1 mL in THF, 1 mol% Co-NP, 2 bar H2, 20 °C, 3 h. If not otherwise noted, yields were determined by GC-FID vs. internal n-pentadecane.[14]

functionalized, and tetra-substituted alkenes required slightly harsher conditions. Good chemoselectivities were observed for bifunctional molecules such as limonene, 2-vinylpyridine. Functional group tolerance tests (Figure S1) showed that cyano, nitro, and carbonyl functions were detrimental to the reaction, while esters, ethers, amines, fluoro and chloro groups were tolerated.[14]

The catalytic protocol was further simplified by preparing nanoparticles *in situ* via the standard protocol but without laborious work-up and isolation procedures. Control experiments showed the identical catalytic activity (Figure S2) and long-term stability of *in situ* prepared Co-NPs and the isolated Co-NPs (Table 1). Magnetic separation also afforded active Co(0) nanoparticles (mCo-NP) with identical catalytic activity (Figure S2) that could be easily recycled over multiple runs (Figure 3). The decoration of nanoparticles with organic surfactants is a versatile method for alteration of the surface properties and introduction of functionalities.6,[23] The addition of oleylamine (1.5 equiv. per Co) to the freshly prepared nanoparticles resulted in the formation of a very stable, highly

Table 1 Comparison of different Co-NP catalysts and ageing periods.

Substrate	[Co]	Yield [%] after 1 week	Yield [%] after 6-35 weeks
(phenyl vinyl)	Co-NP	>99	>99
	mCo-NP	>99	98
	in situ Co-NP	>99	97
	aCo-NP	66 (69)	3 (8)
C_9H_{19}	Co-NP	96	98
	mCo-NP	>99	96
	in situ Co-NP	>99	96
	aCo-NP	>99	91

Conditions: 0.5 mmol substrate, 2 mL THF, yields were determined by quantitative GC-FID vs. internal *n*-pentadecane. Conversion in parentheses if not >95%. [a]35 weeks. [b]9 weeks. [c] 6 weeks.

dispersed nanoparticle suspension (aCo-NP) that could not be magnetically separated by a standard magnet. The oleylamine-supported aCo-NP were catalytically less active (Figure S2) and less stable than the amine-free Co-NPs so that there is no benefit of surfactant addition to Co-NP catalysis under these conditions (Table 1).

The standard reaction conditions enabled effective catalyst recycling after each reaction run by an external magnet without loss of catalyst material and activity (Figure 3). More than 99.6% of the particles were removed from the organic phase by a commercial Nd magnet (10x20 mm, N45) and decantation (Figure 3b,c). ICP-OES studies documented minimal leaching (<0.4% Co, <0.02 mol%) into the liquid phase after the first run. After filtering the decanted reaction solution over silica, an insignificant amount of cobalt (0.68 ppm per Co supplied) remained in the organic phase.[14] TEM images showed only marginal differences of particle topology between the Co catalysts (Co-NPs and *in situ* Co-NPs) before and after the hydrogenations (Figures S4–S7). Multiple

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sequential reactions were performed with the same catalyst portion. Importantly, ultrasonication of the catalyst suspension resulted in a healing of catalytic activity after multiple recycling operations (>10) and when the catalyst aged during storage for extended periods (several days).

Proof of the heterogeneous nature of the catalyst was also derived from kinetic poisoning experiments (Figure 4).[16] Addition of the selective homotopic poison dibenzo[*a,e*]cyclooctatetraene (dct)[16,24] at 40% conversion of a model hydrogenation did not change the reaction rate. Consistently, complete inhibition resulted from the addition of mercury (300 equiv. per Co). This quantitative amalgamation was accompanied by decolorization and formation of a metallic

Figure 3 a) Consecutive hydrogenation runs of styrene (0.5 mmol) using the same catalyst particles (5 mol%) and regeneration of catalyst activity by ultrasonication (box). Yields (black), conversions (red). b) Suspension of the hydrogenation reaction of styrene with 5 mol% Co-NP. c) Catalyst separation by an external magnet (after 1 min).

Figure 4 Catalyst poisoning with dct (2 equiv. per Co), PMe$_3$ (0.1 equiv. per Co), Hg (300 equiv. per Co). Yields were determined from the H$_2$ consumption.

mercury drop with silvery luster at the bottom of the reaction.[25] An identical reaction ceased immediately after addition of a 0.1 equiv. PMe$_3$ per Co. Lower amounts of PMe$_3$

(0.025 equiv.) resulted in partial catalyst poisoning. These studies provide strong indications of a heterotopic mechanism in full accord with literature reports.[16] Finally, we extended the substrate scope of our nanoparticles beyond alkene hydrogenations to imines and heteroaromatic quinolines. Homogeneous and heterogeneous 3d metals that catalyze imine and quinoline hydrogenation are still relatively scarce even though such hydrogenations are an attractive, atom-economic route to amines, while compounds with a 1,2,3,4-tetrahydroquinoline scaffold are found in natural products and bioactive compounds.[26] Gratifyingly, our Co-NP catalysts were active in the clean hydrogenation of small and bulky aldimines, ketimines, and various quinolines (Figure 5). Chloro, ester, hydroxyl, benzyl, furan, and pyridine, functions were tolerated. Besides the hydrogenation of the imine, the furanyl and pyridyl imines underwent partial hydrogenation of the heterocycle.[14]
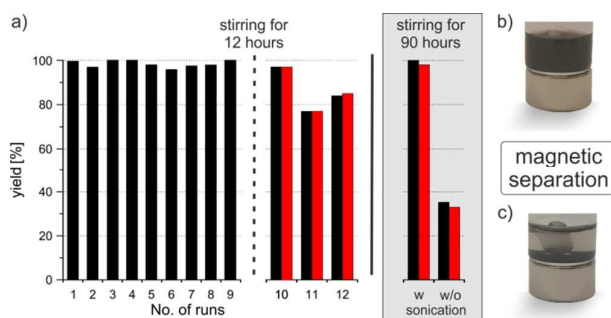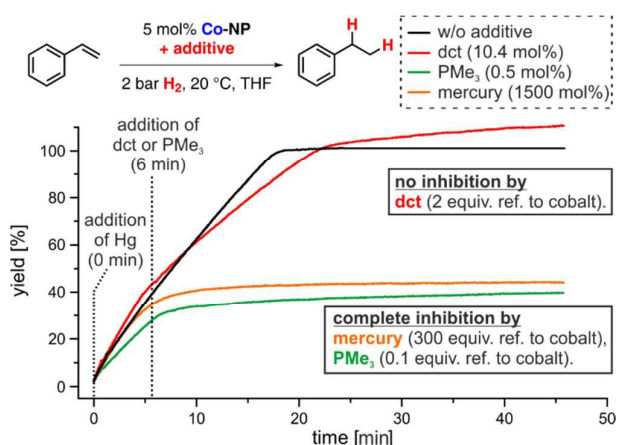
Conclusions

In summary, we have established a straightforward and operationally simple synthesis of quasi-naked, colloidally and chemically stable Co(0) nanoparticles from commercial reagents. Detailed analytical studies (TEM, XRD, DLS, poisoning) documented the heterogeneous nature of the small and uniform nanoparticles of 3.4±0.4 nm. Applications to catalytic hydrogenations enabled the clean conversion of alkenes, alkynes, imines, and quinolines under mild conditions (2 – 20 bar H$_2$, 20 – 80 °C). The catalysts could be easily mechanically separated and recycled for multiple hydrogenation runs without loss of activity. The ease of synthetic preparation in the absence of complex ligands, their wide catalytic applicability, the facile catalyst recycling and long-term stability constitute prime advantages of such cobalt catalysts that should stimulate further use in the realm of organic synthesis.

Acknowledgments

Conflicts of interest

There are no conflicts to declare.

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5 mol% Co-NP, 10-20 bar H$_2$, THF, 60-80°C, 3-24 h[14]

2a: R = H: 91 (isol.)
2b: R = CO$_2$Me: 83 (isol.)

2c: 88 (isol.)

2d: 98 (isol.)

2e: R = Ph: 99 (isol.)
2f: R = Cy: 67 (isol.)

2g: 84 (isol.)

2h: 63 (isol.)

2i: 92 (isol.)

2j: 96 (isol.)

2k: 89 (isol.)

2l: 99 (isol.)

2m: 73 (isol.)

2n: 39 (isol.)

2o: 77 (isol.)

2p: 62 (isol.)

2q: 98 (isol.)
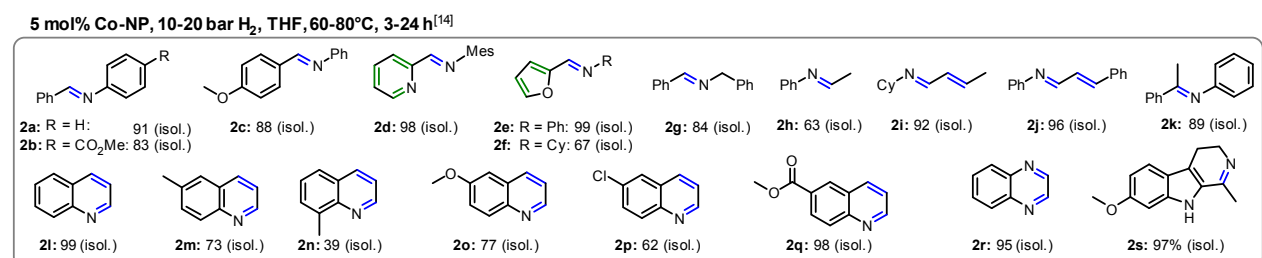
2r: 95 (isol.)

2s: 97% (isol.)

Figure 5 Co-catalyzed hydrogenation of imines and quinolines. Blue bonds are sites of hydrogenation. Green bonds indicate traces of overhydrogenation. Standard conditions: 0.5 mmol substrate, 2 mL THF, 5 mol% Co-NP, 10 bar H2, 60 °C, 24 h. If not otherwise noted, yields were determined by GC-FID vs. n-pentadecane.[14]

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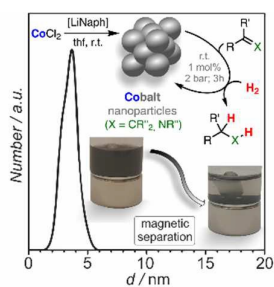
Small Co(0) nanoparticles catalyze hydrogenations of alkenes, alkynes, imines, and heteroarenes; the magnetic properties enabled catalyst separation and multiple recyclings.