

Nanoparticle Catalysts

A General Catalyst Based on Cobalt Core–Shell Nanoparticles for the Hydrogenation of N-Heteroarenes Including Pyridines

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In memory of Professors B. S. Sheshadri and S. M. Mayanna, former Chairmen of the Chemistry Department, Bangalore University, India

Abstract: Herein, we report the synthesis of specific silica-supported Co/Co₃O₄ core–shell based nanoparticles prepared by template synthesis of cobalt-pyromellitic acid on silica and subsequent pyrolysis. The optimal catalyst material allows for general and selective hydrogenation of pyridines, quinolines, and other heteroarenes including acridine, phenanthroline, naphthyridine, quinoxaline, imidazo[1,2-a]pyridine, and indole under comparably mild reaction conditions. In addition, recycling of these Co nanoparticles and their ability for dehydrogenation catalysis are showcased.

The catalytic hydrogenation of N-heteroarenes represents an atom-efficient methodology to access aliphatic cyclic amines, which are of interest for basic organic synthesis, drug discovery, material sciences, and alternative energy technologies.^[1] In particular, piperidines and 1,2,3,4-tetrahydroquinolines are integral parts of pharmaceuticals, agrochemicals, biomolecules, and natural products.^[1a,c,g] For these products, the catalytic hydrogenation of pyridines^[2,3] and quinolines^[3a,4–7] offers a straightforward approach compared to typically applied multistep procedures.^[1a,c] However, catalyst deactivation might occur easily due to the interaction of nitrogen moiety of substrates or products with the supported metal centers.^[8] In this respect, the hydrogenation of pyridines is known to be particularly challenging. Hence, this reaction mainly relies on precious-metal-based catalysts.^[2a–b,e–g,3e,n] In addition, a cobalt-based heterogeneous catalyst is known; however, it requires drastic conditions limiting its applicability (160 °C, 60 bar H₂).^[3o] On the other hand, for the facile hydrogenation of quinolones and related N-heteroarenes, several non-noble homogeneous^[5] and heterogeneous^[7] catalysts based on Fe,^[7a] Co,^[7b–e,h] Ni,^[7f] and Mn^[7g] have been

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successfully developed complementary to state-of-the-art precious metal catalysts.^[6] Despite these achievements, still the development of a general and selective non-noble metal based catalyst for the hydrogenation of N-heteroarenes including pyridines under milder reaction conditions continues to be of scientific interest and is challenging.

The preparation of active supported nanoparticles depends strongly on the use of appropriate precursors and optimized preparation techniques. Compared to the thermal or chemical reduction of simple metal salts,^[9] the template synthesis of metal–organic frameworks (MOFs) or coordination polymers (CPs) on a solid support and subsequent pyrolysis offers an alternative approach, which has become highly attractive in recent years.^[10] Advantageously, a plethora of relatively inexpensive and stable organic ligands are commercially available to prepare MOFs or CPs, which can be used as precursors to synthesize diverse nanomaterials. As an example, we^[10d,i] and others^[10e–h] reported the use of cobalt MOFs and CPs, obtained from diamines and di- or tetracarboxylic acids, as appropriate precursors for the preparation of supported nanoparticles for redox reactions. Based on this work, herein we report the preparation of silica-supported Co/Co₃O₄ core–shell nanoparticles by immobilization and pyrolysis of cobalt-pyromellitic acid template on commercial silica (Figure 1). Catalytic investigations revealed the superiority of these novel supported nanoparticles for the hydrogenation of pyridines, quinolines, and other different N-heteroarenes.

Aromatic carboxylic acids are key building blocks for the formation of MOFs and metal-containing coordination polymers (MCPs).^[11] Based on their use, new innovative materials have been introduced in the past two decades, which showed interesting performances, especially in separation technologies.^[11] In contrast, relatively few applications of such materials have been demonstrated in modern catalysis, despite significant efforts.^[10d,i,e–h] On the other hand, it has been demonstrated that pyrolysis of MOFs or MCPs can lead to stable supported nanoparticles with unique structures. For example, the pyrolysis of cobalt-MOF on carbon and silica led

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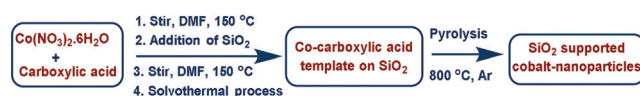


Figure 1. Preparation of cobalt nanoparticles by pyrolysis of Co-carboxylic acid templates on SiO₂.

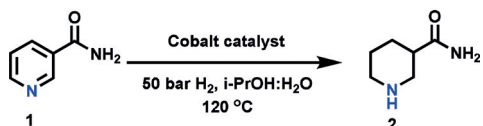
to general reductive amination and arene hydrogenation catalysts.^[10d,i]

Based on this and related work,^[10d,j] we became interested in studying the behavior of supported cobalt nanoparticles prepared from cobalt salts of different carboxylic acids. For this purpose, a cobalt salt was mixed with a set of four model carboxylic acids, which have been used as common organic linkers for the preparation of MOFs. Specifically, benzoic acid, terephthalic acid, trimesic acid (1,3,5-benzenetricarboxylic acid), or pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) were stirred with cobalt(II) nitrate hexahydrate in DMF at 150 °C.^[10j] To these in situ generated materials, Aerosil silica was added and the whole mixture was stirred again at the same temperature for another 4–5 h. After slow evaporation of the solvent, followed by drying, the templated materials (Co-carboxylic acid@SiO₂) were obtained as colored solids. Subsequent pyrolysis at 800 °C under argon for 2 h led to different cobalt nanoparticles supported on silica (Figure 1).

All the materials were tested for liquid-phase hydrogenation of nicotinamide (**1**) at 120 °C and 50 bar of hydrogen. This benchmark reaction was chosen due to the difficult nature of hydrogenation of pyridines (vide supra) and the intrinsic chemoselectivity problem. Moreover, due to the biochemical relevance of nicotinamide as part of coenzymes, its catalytic hydrogenation is also considered to be interesting.

Among the prepared materials, the cobalt-pyromellitic acid on silica at 800 °C constitutes the most active and selective catalyst (Co-pyromellitic acid@SiO₂-800), which allowed for the complete hydrogenation of nicotinamide (**1**) and produced the desired product, nipecotamide (**2**) in 97 % yield. Notably, there is strong influence on catalysis depending on the carboxylic acid linker used. Benzoic acid resulted in a completely inactive material, while other di-, tri-, and tetracarboxylic acids gave active catalysts (Table 1, entries 1–4). Comparison experiments in the presence of simple cobalt(II) nitrate or a mixture of it and pyromellitic acid

Table 1: Hydrogenation of nicotinamide: activity of different cobalt catalysts.



Entry	Catalyst	Conv. [%]	Yield [%]
1 ^[a]	Co-benzoic acid@SiO ₂ -800	< 3	< 2
2 ^[a]	Co-terephthalic acid @SiO ₂ -800	65	63
3 ^[a]	Co- trimesic acid @SiO ₂ -800	75	73
4 ^[a]	Co-pyromellitic acid@SiO ₂	> 99	97
5 ^[a]	Co(NO ₃) ₂ @SiO ₂ -800	< 2	< 1
6 ^[a]	Co-pyromellitic acid@SiO ₂	< 2	< 1
7 ^[a]	Co(NO ₃) ₂ @SiO ₂	–	–
8 ^[b]	Co(NO ₃) ₂ ·6 H ₂ O + pyromellitic acid	–	–
9 ^[b]	Co(NO ₃) ₂ ·6 H ₂ O	–	–

Reaction conditions: [a] 0.5 mmol nicotinamide, weight of catalyst corresponds to 40 mg catalyst (7.5 mol % Co), 50 bar H₂, 3 mL solvent (i-PrOH: H₂O; 2:1), 120 °C, 24 h. Yields were determined by GC using *n*-hexadecane as standard. [b] 0.5 mmol substrate, 7.5 mol % Co-(NO₃)₂·6 H₂O, 7.5 mol % of pyromellitic acid, 50 bar H₂, 3 mL solvent (i-PrOH:H₂O; 2:1), 120 °C, 24 h yields were determined by GC using *n*-hexadecane standard.

were carried out and showed that both are inactive, too. Similarly, nonpyrolyzed and pyrolyzed cobalt(II) nitrate on silica as well as nonpyrolyzed Co-pyromellitic acid on silica were also not active (Table 1, entries 6–8).

To understand the superior activity of Co-pyromellitic acid@SiO₂-800, detailed structural characterization of this material was performed using X-ray powder diffraction (XRD), scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) techniques.^[10j] XRD analysis of Co-pyromellitic acid@SiO₂-800 showed the presence of both metallic and oxidic cobalt phases (Co and Co₃O₄) (Figure S1). In the case of Co(NO₃)₂@SiO₂-800, only the presence of the oxidic cobalt phase was observed (Figure S2).

STEM analysis of the most active catalyst also revealed the formation of particles consisting of metallic Co and different Co oxides (Co₃O₄) with sizes in the range of about 10–20 nm (Figure 2 and Figures S3 and S4). Many of these particles are of core–shell structure, where the core consists of metallic Co with an oxide shell as indicated by HAADF (Figure 2, center and right). The oxide shells and purely oxide particles are usually polycrystalline. Next, XPS analysis of the most active catalyst was performed to identify the nature of cobalt species at the surface of the material. More specifically, deconvolution of Co 2p peaks confirmed the presence of mixed oxidation for Co (Co 2p_{3/2} in Co⁰: 778.49 eV; Co²⁺: 779.92 eV) (Figure S9). Although a peak for Co³⁺ could not be deconvoluted, the presence of strong satellite peaks at 786.43 eV and 802.20 eV is indicative for multiple oxidized Co species, as satellite peaks arise due to spin–spin interactions of different Co species.^[12]

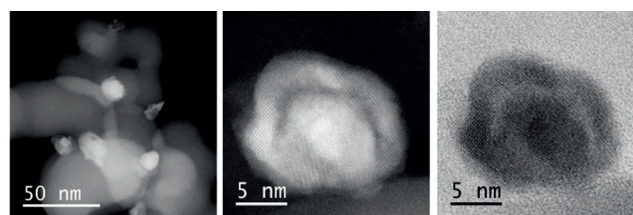
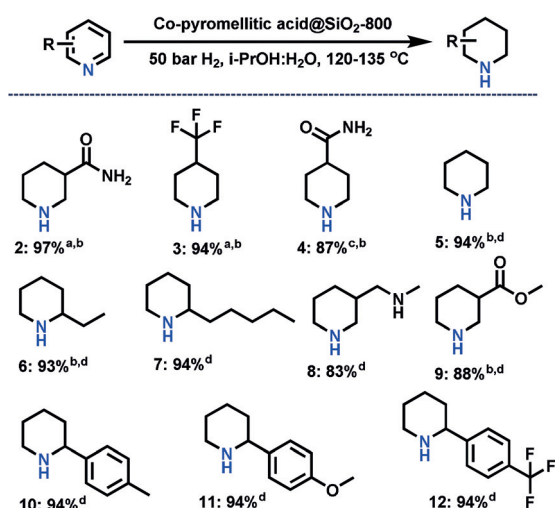


Figure 2. STEM-HAADF (left and center) and -ABF (right) images of Co-pyromellitic acid @SiO₂-800 catalyst.

With a successful catalyst for the hydrogenation of nicotinamide in hand, we explored its applicability for different N-heteroarenes. As shown in Schemes 1–3, a series of substituted and functionalized pyridines and quinolines as well as other heteroarenes underwent complete or partial hydrogenation to produce cyclic aliphatic derivatives in good to excellent yields.

Noteworthy, simple pyridine was efficiently hydrogenated and produced the parent piperidine in excellent yield (product **5**). Substituted pyridines with both electron-donating and -withdrawing groups were hydrogenated to give the corresponding products in up to 94 % yields (Scheme 1). Interestingly, the catalyst system preferentially reduces the N-heteroarene ring in the presence of other reducible groups such as amide and ester (products **2**, **3**, **9**). Similarly, the presence of substituted arene rings is tolerated (products **10**–**12**).



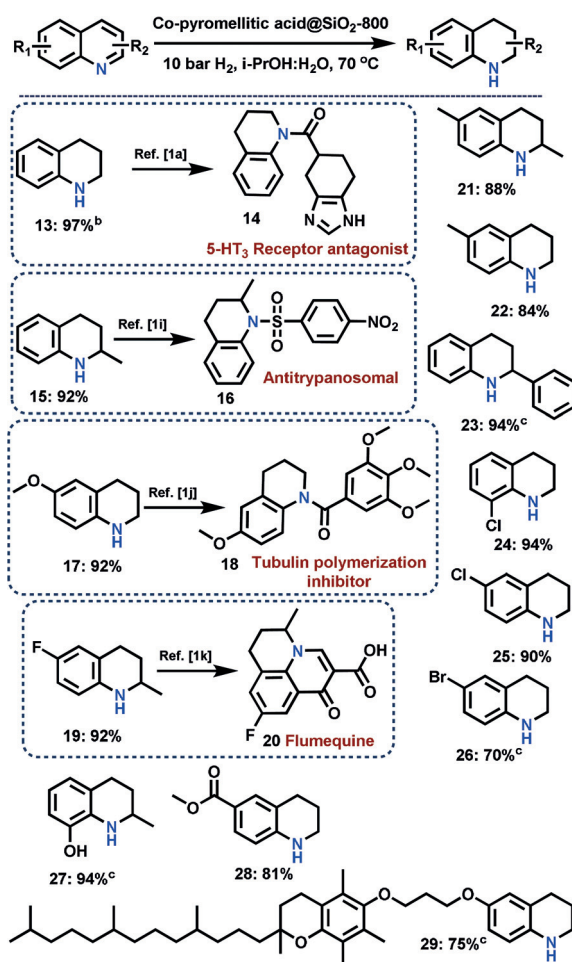
Scheme 1. Hydrogenation of pyridines catalyzed by Co-pyromellitic acid@SiO₂-800.^[a] Reaction conditions: [a] 0.5 mmol substrate, 40 mg catalyst (7.5 mol% Co), 50 bar H₂, 3 mL (i-PrOH:H₂O; 2:1), 120 °C, 24 h, yields of isolated products. [b] Yields were determined by GC using *n*-hexadecane standard. [c] Same conditions as [a] but with 50 mg catalyst. [d] Same conditions as [a] but with 60 mg catalyst at 135 °C for 48 h.

Next, we applied this cobalt catalyst for the hydrogenation of quinolines (Scheme 2). As a result, nine quinolines were hydrogenated under comparably mild conditions (70 °C, 10 bar of hydrogen) and 1,2,3,4-tetrahydroquinolines were produced in up to 97% yield (products **13**, **15**, **17**, **19**, **21**, **22**, **24**, **25**, and **28**). Here, sensitive substituents (Br, Cl) and functional groups such as hydroxyl, ether, and ester groups were well tolerated (products **19**, **24**–**29**). Notably, some of the tetrahydroquinolines presented in Scheme 2 serve as precursors/intermediates for the preparation of bioactive molecules. Specifically, the preparation of products **14**, **16**, **18**, **20** and **29** resulted in 5-HT₃ receptor antagonist, antitrypanosomal drug, tubulin polymerization inhibitor, flumequine, and tocopherol derivatives.

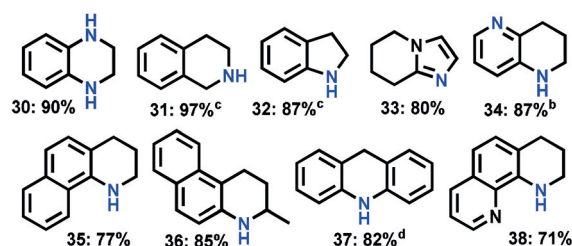
Following the hydrogenation of pyridines and quinolines, the reduction of other N-heteroarenes such as quinoxaline, indole, imidazo[1,2-*a*]pyridine, 1,5-naphthyridine, acridines, and phenanthroline was performed (Scheme 3). Again, in all these cases the N-heteroarene rings were selectively reduced and the corresponding partially reduced products were obtained in up to 97% yield.

To prove the synthetic utility and practicability of the general hydrogenation procedure, several reactions were completed on 0.5–1 g scale (Figure S11). In addition, this catalyst can be conveniently recycled and reused up to six times without significant loss in the activity or selectivity (Figure S12). STEM analysis of catalyst samples after one and seven reuses showed a partial re-dispersion of cobalt into a thin layer of Co-oxide on the surface of the support progressing with the number of uses (Figures S5–S8).

Finally, the optimal catalyst was also tested for the reverse dehydrogenation process. Because of the microreversibility of the individual catalytic steps, such a transformation should be also possible. Indeed, in presence of Co-pyromellitic acid@-

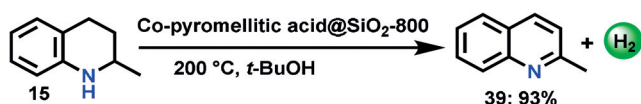


Scheme 2. Synthesis of tetrahydroquinolines catalyzed by Co-pyromellitic acid@SiO₂-800. Reaction conditions: [a] 0.5 mmol substrate, 50 mg Co-pyromellitic acid@SiO₂-800, (9 mol% Co), 10 bar H₂, 3 mL (i-PrOH:H₂O; 2:1), 70 °C, 24 h, yields of isolated products. [b] Yields were determined by GC using *n*-hexadecane standard. [c] Same conditions as [a] but at 120 °C with 30 bar H₂.



Scheme 3. Selective hydrogenation of different N-heteroarenes using Co-pyromellitic acid@SiO₂-800. Reaction conditions: [a] 0.5 mmol substrate, 50 mg Co-pyromellitic acid@SiO₂-800, 50 bar H₂, 3 mL (i-PrOH:H₂O; 2:1), 120 °C, 24 h, yields of isolated products. [b] Same conditions as [a] but at 135 °C and 48 h. [c] Yields were determined by GC using *n*-hexadecane standard. [d] Same conditions as [a] but using *t*-BuOH as solvent.

SiO₂-800, 2-methyl-1,2,3,4-tetrahydroquinoline underwent dehydrogenation and provided 2-methylquinoline in 93% yield (Scheme 4). Such reactions are of general interest in the context of liquid organic hydrogen carriers (LOHC) technologies.^[13]



Scheme 4. Dehydrogenation reaction catalyzed by cobalt nanoparticles. Reaction conditions: 2 mmol substrate, 240 mg catalyst (11 mol % Co), 10 mL *t*-BuOH, 200 °C, 48 h, GC yield using *n*-hexadecane standard.

In conclusion, we report the preparation of novel supported Co/Co₃O₄ core-shell nanoparticles by template synthesis of Co-pyromellitic acid on silica and subsequent pyrolysis. These particles are shown to be active for general hydrogenation of variety of N-heteroarenes including pyridines, quinolines, acridine, phenanthroline, naphthyridine, quinoxaline, imidazo[1,2-*a*]pyridine, and indole. In addition, we believe this or similar catalysts also offer opportunities for other hydrogenation and dehydrogenation processes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Co nanoparticles · hydrogenation · N-heteroarenes · pyridines · quinolines

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