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# A General Catalyst based on Cobalt Core-shell Nanoparticles for Hydrogenation of *N*-Heteroarenes including Pyridines

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In memory of Profs. 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/Co<sub>3</sub>O<sub>4</sub> 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 Conanoparticles 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.<sup>[1]</sup> In particular, piperidines and 1,2,3,4-tetrahydroquinolines are integral parts of pharmaceuticals, agrochemicals, biomolecules and natural products.<sup>[1a,c,g]</sup> For these products the catalytic hydrogenation of pyridines<sup>[2-3]</sup> and guinolines<sup>[4-7,3n]</sup> offers a straightforward approach compared to typically applied multistep procedures.<sup>[1a,c]</sup> However, catalyst deactivation might occur easily due to the interaction of nitrogen moiety of substrate or products with the supported metal centers.<sup>[8]</sup> In this respect, the hydrogenation of pyridines is known to be particularly challenging. Hence, this reaction mainly relies on precious metal-based catalysts.<sup>[2a,b,e-g,3e,3n]</sup> In addition, a cobalt-based heterogeneous catalyst is known; however it requires drastic conditions limiting its applicability (160 °C, 60 bar H<sub>2</sub>).<sup>[30]</sup> On the other hand, for the easier hydrogenation of quinolones and related N-heteroarenes several non-noble homogeneous<sup>[5]</sup> and heterogeneous<sup>[7]</sup> catalysts based on Fe<sup>[7a]</sup>, Co<sup>[7b-e,h]</sup>, Ni<sup>[7f]</sup> and Mn<sup>[7i]</sup> have been successfully developed complementary to state-of the-art precious metal catalysts.<sup>[6]</sup> Despite these achievements, still the development of a general and selective non-noble metal based catalyst for the hydrogenation of Nheteroarenes including pyridines that work 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 thermal or chemical reduction of simple metal salts<sup>[9]</sup>, the template synthesis of metal organic frameworks (MOFs) or coordination polymers (CPs) on a solid support and subsequent pyrolysis offers an alternative approach, which became highly attractive in recent years.<sup>[10]</sup> Advantageously, a plethora of relatively inexpensive and stable organic ligands are commercially available to prepare or MOFs or CPs, which can be used as precursors to synthesize diverse nanomaterials. As an example, we<sup>[10d,i]</sup> and others.<sup>[10e-h]</sup> 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 these works, herein we report the preparation of silica supported Co/Co<sub>3</sub>O<sub>4</sub> core-shell nanoparticles by immobilization and pyrolysis of cobalt-pyromellitic acid template on commercial silica (Fig. 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 metal organic frameworks (MOFs) and metalcontaining coordination polymers (MCPs). <sup>[11]</sup> Based on their use, new innovative materials were introduced in the past two decades, which showed interesting performances, especially in separation technologies.<sup>[11]</sup> In contrast, relatively few applications of such materials have been demonstrated in modern catalysis, despite significant efforts.<sup>[10d,i, e-h]</sup> 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 to general reductive amination and arene hydrogenation catalysts.<sup>[10d,i]</sup>

Based on this and related work, [10d,i] we became interested to study 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 MOF's. Specifically, benzoic acid, terephthalic trimesic acid (1,3,5-benzenetricarboxylic acid), acid. or pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) were stirred with cobalt(II) nitrate hexahydrate in DMF at 150 °C.[10i] To these in situ-generated materials, Aerosil® 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@SiO<sub>2</sub>) were obtained as colored solids. Subsequent pyrolysis at 800 °C under argon for 2h led to different cobalt nanoparticles supported on silica (Fig. 1).



Fig. 1. Preparation of cobalt-nanoparticles by pyrolysis of Co-carboxylic acid templates on  $\text{SiO}_2.$ 

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 biochemical relevance of nicotinamide, as part of coenzymes, its catalytic hydrogenation is also considered to be interesting.

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Among the prepared materials, the cobalt-pyromellitic acid on silica at 800 °C constitutes the most active and selective catalyst (Co-pyromellitic acid@SiO<sub>2</sub>-800), which allowed for the complete hydrogenation of nicotinamide (1) and produced 97% of desired product, nipecotamide (2). Notably, there is strong influence on catalysis depending on the used carboxylic acid linker. Benzoic acid resulted in a completely inactive material, while other di-, tri-, and tetra-carboxylic acids gave active catalysts (Table 1; entries1-4). Comparison experiments in the presence of simple cobalt(II) nitrate or a mixture of it and pyromellitic acid were carried out and showed that both are inactive, too. Similarly, non-pyrolyzed and pyrolyzed cobalt(II) nitrate on silica as well as non-pyrolyzed Co-pyromellitic acid on silica were also not active (Table 1, entries 6-8).

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

	O Cobalt catalyst	_ ہٹ	NH <sub>2</sub>
	50 bar H₂, i-PrOH:H₂O 120 ℃		
Entry	Catalyst	Conv. (%)	Yield (%)
1 <sup>[a]</sup>	Co-benzoic acid@SiO2-800	<3	<2
2 <sup>[a]</sup>	Co-terephthalic acid @SiO2-800	65	63
3 <sup>[a]</sup>	Co- trimesic acid @SiO <sub>2</sub> -800	75	73
4 <sup>[a]</sup>	Co-pyromellitic acid@SiO <sub>2</sub>	>99	97
5 <sup>[a]</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> @SiO <sub>2</sub> -800	<2	<1
6 <sup>[a]</sup>	Co-pyromellitic acid@SiO <sub>2</sub>	<2	<1
7 <sup>[a]</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> @SiO <sub>2</sub>	-	
8 <sup>[b]</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + pyromellitic acid	-	-
9 <sup>[b]</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	-	

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

To understand the superior activity of Co-pyromellitic acid@SiO<sub>2</sub>-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.<sup>[10i]</sup> XRD of Co-pyromellitic acid@SiO<sub>2</sub>-800 showed the presence of both metallic and oxidic cobalt phases (Co and Co<sub>3</sub>O<sub>4</sub>) (Fig. S1). In case of Co(NO<sub>3</sub>)<sub>2</sub>@SiO<sub>2</sub>-800, only the presence of the oxidic cobalt phase was observed (Fig. S2).

STEM analysis of the most active catalyst also revealed the formation of particles consisting of metallic Co and different Co oxides ( $Co_3O_4$ ) with sizes in the range of about 10-20 nm (Fig. 2 and Figs. S3-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 (Fig. 2; center and right). The oxide shells and purely oxide particles are usually polycrystalline. Next, XPS analysis of most active catalyst was performed to

identify the nature of cobalt species at the surface of the material. More specifically, deconvolution of Co2p peaks confirmed the presence of mixed oxidation for Co (Co2p3/2 in Co(0): 778.49 eV; Co<sup>2+</sup>: 779.92 eV) (Fig. S9). Although a peak for Co<sup>3+</sup> could not be deconvoluted, the presence of strong satellite peaks at 786.43 eV and 802.20 eV are indicative for multiple oxidized Co species as satellite peaks arise due to spin-spin interactions of different Co-species.<sup>[12]</sup>



Figure 2. STEM-HAADF (left and center) and -ABF (right) images of Co-pyromellitic acid  $@\,SiO_2{\text{-}}800$  catalyst.

After having 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 cycle aliphatic derivatives in good to excellent yields.



Co-pyromellitic acid@SiO<sub>2</sub>-800 catalyzed hydrogenation of pyridines<sup>[a]</sup>. Reaction conditions: [a] 0.5 mmol substrate, 40 mg catalyst (7.5 mol% Co), 50 bar H<sub>2</sub>, 3 mL (i-PrOH:H<sub>2</sub>O; 2:1), 120 °C, 24h, isolated yields. [b] Yields were determined by GC using n-hexadecane standard. [c] Same as [a] with 50 mg catalyst. [d] Same as [a] with 60 mg catalyst at 135 °C for 48h.

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 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).

Next, we applied this cobalt-catalyst for the hydrogenation of quinolines (Scheme 2). As a result, 9 quinolines were semihydrogenated under comparably mild conditions (70 °C, 10 bar of hydrogen) and produced 1,2,3,4-tetrahydroquinolines in up to 97% yields (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 terahydroquinolines presented in Scheme 2 serve as precursors/intermediates for the preparation of bio-active 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.



After having performed 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 were performed (Scheme 3). Again, in all these cases the *N*-heteroarene rings were selectively reduced and gave the corresponding partially reduced products in up to 97% yields.



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

To prove the synthetic utility and practicability of the general hydrogenation procedure, several reactions were completed on 0.5-1 g-scale (Fig. S11). In addition, this catalyst can be conveniently recycled and reused up to six times without significant loss in the activity or selectivity (Fig. 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 (Figs. S5-S8).

Finally, the optimal catalyst was also tested for the reverse dehydrogenation process. Because of the micro-reversibility of the individual catalytic steps such transformation should be also possible. Indeed, in presence of Co-pyromellitic acid@SiO<sub>2</sub>-800, 2-methyl-1,2,3,4-tetrahydroquinoline underwent dehydrogenation and yielded 93% of 2-methylquinoline (Scheme 4). Such reactions are of general interest in the context of liquid organic hydrogen carriers (LOHC) technologies.<sup>[13]</sup>



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

In conclusion, we report the preparation of novel supported  $Co/Co_3O_4$  core-shell nanoparticles by template synthesis of Copyromellitic 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**: N-heteroarenes • Co-nanoparticles • hydrogenations • pyridines • quinolines •

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#### **Entry for the Table of Contents**

#### COMMUNICATION





One fits all: Development of a general hydrogenation catalyst for N-heteroarenes: Co/Co<sub>3</sub>O<sub>4</sub> core-shell nanoparticles prepared by pyrolysis of Co-pyromellitic acid template on silica resulted in stable and reusable catalysts for the selective hydrogenation of pyridines, quinolines and other heteroarenes.

A General Catalyst based on Cobaltfor **N-Heteroarenes**