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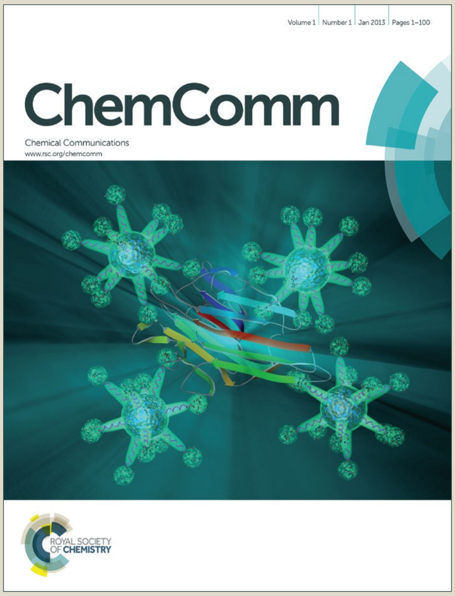

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Transfer Hydrogenation of Unsaturated Bonds in the Absence of Base Additives Catalyzed by a Cobalt-Based Heterogeneous Catalyst

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A novel non-noble Co@C-N catalytic system has been developed for catalytic transfer hydrogenation reactions. Co@C-N was found to be highly active and selective in the hydrogenation of a variety of unsaturated bonds with isopropanol in the absence of base additives.

Transition metal-catalyzed transfer hydrogenation protocols are convenient and alternative green chemical methods to traditional energy-consuming hydrogenation processes, able to provide high atom efficiency and generating advantageous economics.[1] The use of hydrogen donor reagents (e.g. alcohols) in transfer hydrogenation reactions can avoid the use of autoclaves and high-pressure hydrogen, being highly relevant for industrial applications.[2]

Various noble metals (e.g., ruthenium, iridium, and rhodium) have been typically employed in transfer hydrogenation reactions of a number of chemical functionalities including ketones, aldehydes, nitrocompounds and imines.[3] However, most of these systems are largely based on homogeneous organometallic complexes which additionally required the addition of base additives to provide good product yields .[3a-3j]

Noble metal free systems have recently emerged as promising alternative in transfer hydrogenation reactions,[4] including highly effective and soluble Fe,[5] Cu,[6] Zn,[7] and Co[8] complexes. Similarly, the majority of the reported catalytic systems required base additives[5b-5l] or/and homogeneous phosphorus-containing ligands.[5a-5f,6] Significant improvements are therefore desirable to advance in the development of more sustainable, environmentally friendly, and economic catalytic systems in transfer hydrogenation processes.

In continuation with recent research endeavours from the group, here we report the design of non-noble metal-based heterogeneous catalysts for transfer hydrogenation reactions of various unsaturated bonds catalyzed in the absence of any base additives. The catalysts were prepared using a Co-containing metal-organic framework (MOF) as sacrificial template and the reactions were conducted using *i*-PrOH as hydrogen donating solvent. The choice of the Co-MOF as template relates to the presence of triethylenediamine basic sites (even after simple thermolysis) which could be favorable for transfer hydrogenation reactions. To the best of our knowledge, there are currently no reports on the use of MOF-derived metal/carbon nano-composites for transfer hydrogenation.

Multiple advantages of the proposed catalytic system include a remarkable versatility not only for $C=O$ hydrogenation (including ketones and aldehydes) but also for $C=C$, $C\equiv N$, and $N=O$ bonds), an environmental-benign protocol (reactions conducted in a neutral environment under mild reaction conditions) and the use of a magnetically separable non-noble metal catalyst in a simple and safe reaction setup (in the absence of molecular hydrogen, under easy operation and facile separation owing to the magnetic nature of the Co system).

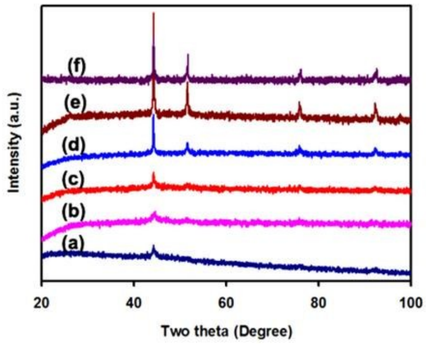

Figure 1. Powder XRD patterns of the Co@C-N samples: (a) Co@C-N-500-15h, (b) Co@C-N-600-15h, (c) Co@C-N-700-15h, (d) Co@C-N-800-15h, (e) Co@C-N-900-15h, and (f) Co@C-N-900-15h after reaction.

The powder X-ray Diffraction (XRD) patterns of Co-MOF (Fig. S1) matched well with those reported in literature,[9] confirming the structure of the as-synthesized MOF material in this work (see the SI for the preparation of the MOF). Thermogravimetric Analysis (TGA) curves (Fig. S2) showed that the Co-MOF was stable at temperatures around 400 ℃.[10]

Co@C-N-X-T was prepared after Co-MOF pyrolysis (here X and T represent thermolysis temperature and time, respectively). XRD patterns of Co@C-N-X-T materials (Fig. 1 and Fig. S3) exhibited five diffraction peaks at around 44.3°, 51.6°, 76.1°, 92.3°, and 97.9°, respectively, characteristics of metallic Co (JCPDS No. 15-0806). Co diffraction peaks showed improved intensity for materials prepared at higher pyrolysis temperatures with longer times owing to the higher crystallization degree of Co.

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As shown by the N_2 adsorption/desorption isotherms and pore distribution, micropores were only present in Co-MOF (Fig. S4 and Table S1). After thermolysis, the observation of hysteresis loops at higher P/P_0 indicated the presence of mesopores in Co@C-N-X-T materials (Figs. S5-S6, and Table S1). Co and N contents in Co@C-N-X-T samples were ca. 37-41% and 1.5%, respectively (Table S2).

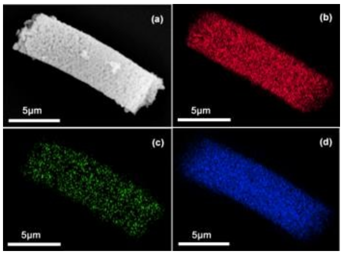

Figure 2. SEM image (a), and elemental mapping of Co@C-N-900-15h: C (b), N (c), Co (d).

The surface morphology of Co@C-N-X-T was subsequently investigated by SEM (Scanning Electron Microscope). As shown in Figs. S7-S8, all Co@C-N exhibited similar particle shapes to those of parent Co-MOF. Moreover, some mesopores could be observed in Co@C-N, with an increasingly rough surface at increasing pyrolysis temperature and time. Elemental mapping (Fig. 2) pointed out a highly uniform distribution of Co, C, and N on the surface of Co@C-N materials.

Transmission Electron Microscopy (TEM) micrographs (Fig. 3 and Fig. S9) revealed Co nanoparticles homogeneously dispersed in Co@C-N materials. Co nanoparticles obtained at higher thermolysis temperatures exhibited relatively larger sizes. The mean particle sizes ranged from 6 nm to 17 nm as the pyrolysis temperature was increased from 500 ^{o}C to 900 ^{o}C.

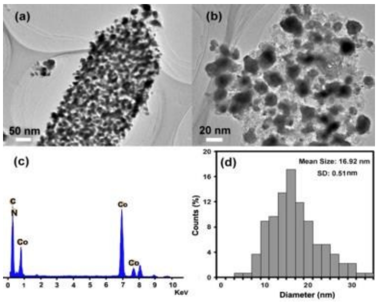

Figure 3. TEM images of Co@C-N-900-15h (a, b), EDS (c), and the corresponding size distribution of Co nanoparticles (d).

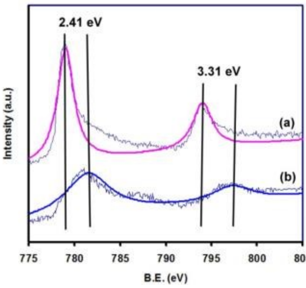

Figure 4. XPS spectra of Co@C-N-900-15h (a) and Co-MOF (b).

X-ray Photoelectron Spectroscopy (XPS) spectra of Co-MOF and Co@C-N-900-15h are shown in Fig. 4. Co@C-N-900-15h exhibited two Co 2p peaks at 778.9 eV and 793.8 eV, which were shifted to lower binding energies (2.4 eV and 3.3 eV, respectively) as compared to those of Co-MOF, indicating that Co(II) in Co-MOF was converted to metallic Co after thermolysis.

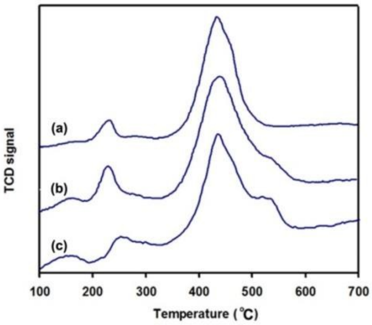

Figure 5. CO_2-TPD profile for (a) Co@C-N-700-15h, (b) Co@C-N-800-15h, and (c) Co@C-N-900-15h.

The basicity of Co@C-N was determined by Temperature Programmed Desorption (TPD) of CO_2, with results depicted in Fig. 5. As the pyrolysis temperature increased, the number of strong basic sites increased with a simultaneously enhanced basicity. Four peaks could be observed (550 ℃, 450 ℃, 250 ℃, and 150 ℃), for Co@C-N-900, which corresponded to the desorption of CO_2 adsorbed on basic sites with different basicity. These basic sites could be related to nitrogen-containing species derived from the triethylenediamine moiety in Co-MOF during thermolysis.

After characterisation, the catalytic activities of the Co@C-N materials were subsequently tested in the transfer hydrogenation of acetophenone to phenethanol as model process. Reactions were performed at 80 ℃ and N_2 atmosphere using isopropanol as both reductant and solvent under base-free conditions. Blank runs (without catalyst) showed no reactivity (Table S3, entry 1). To our delight, as-synthesized Co@C-N materials were highly active for this transformation. Generally, materials prepared under longer thermolysis times and higher temperatures exhibited higher activity and selectivity (Table S3, entries 2-11). Ethyl benzene was the main side product produced in this reaction. Co@C-N-900-15h was found to be the best catalyst among investigated materials in terms of conversion and selectivity to phenethanol (Table S3, entry 6). The amount of isopropanol influenced the activity and selectivity of the reaction (Table S3, entries 12 and 13); i.e., decreasing the quantity of isopropanol to 1 mL resulted in a reduced selectivity for phenethanol while lower conversions were obtained at increasing isopropanol quantities. The reaction also proceeded well at a low catalyst loading (1 mol%), giving 72% conversion with 98% selectivity within 96 h (Table S3, entry 14).

To elucidate the origin of catalytic activity, the metal was removed from Co@C-N-900-15h using aqua regia treatment for 2 days. A reaction run with the metal-free C-N composite gave no conversion, demonstrating the requirement of a metal to catalyze the transfer hydrogenation (Table S3, entry 15). On the other hand, a Co/C material was also essentially not active in this transformation (Table S3, entry 16), which may be related to the lack of basic sites on the carbon support.[5i,5l,11] These results suggest the importance of both a metal (Co) and basic sites in Co@C-N materials to achieve a high catalytic efficiency in transfer hydrogenation.

We further investigated the reusability of Co@C-N-900-15h in the transfer hydrogenation of acetophenone to phenethanol with isopropanol. Results included in Fig. S10 revealed no appreciable loss of conversion or selectivity up to four reaction runs. Powder XRD characterization proved that the structure of catalyst was mostly preserved (Fig. 1), indicating the stability of the material under the investigated conditions.

The scope of the protocol for the transfer hydrogenation of a range of various unsaturated bonds was subsequently investigated under base-free conditions. Firstly, phenyl ketones and cyclohexyl ketones

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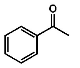
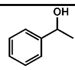
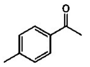
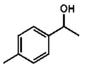
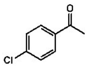
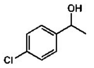
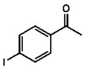
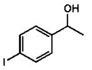
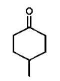
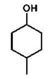
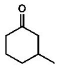
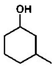
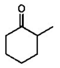
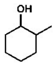
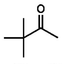
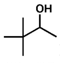
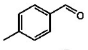
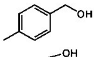
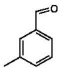
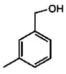
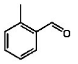
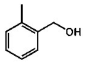
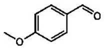
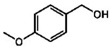
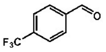
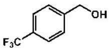
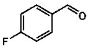
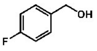
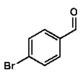
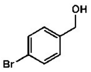
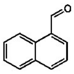
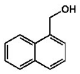
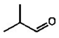
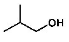
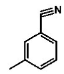
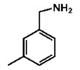
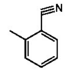
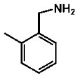
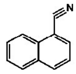
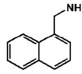
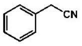
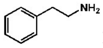
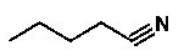
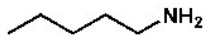
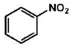
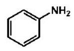
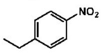
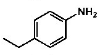
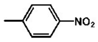
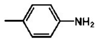
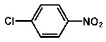
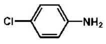
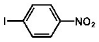
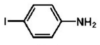
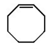
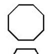
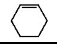
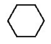
were investigated, which were shown to undergo the transfer hydrogenation with isopropanol to give the corresponding products in quantitative yields (Table 1, entries 2-7). Notably, highly sterically hindered ketones, such as *t*-BuC(O)CH_3, could also be hydrogenated in excellent yields after 60 h reaction (Table 1, entry 8). Aldehydes also worked well, although a slightly longer time and/or higher temperature were required to complete the reactions (Table 1, entries 9-17). In general, electron-rich benzaldehydes exhibited higher activity than electron-deficient ones. For the transfer hydrogenation of benzaldehydes with an electron-withdrawing group such as 4-(trifluoromethyl)benzaldehyde, 4-fluorobenzaldehyde or 4-bromobenzaldehyde, a slight increase in reaction temperature was needed (Table 1, entries 13-15). 1-Naphthalene formaldehyde could also be smoothly hydrogenated in 93% yield (Table 1, entry 16). Aliphatic aldehydes are rarely employed as substrates in transfer hydrogenation owing to the aldol condensation reaction. However, aliphatic aldehydes also underwent transfer hydrogenation under the investigated conditions, affording the desired products in quantitative yields (Table 1, entry 17).

Table 1. Transfer hydrogenation of various substrates with isopropanol [a]

Entry	Substrate	Time (h)	Con. (%)	Sel. (%)
1		17	99	 95
2		12	>99	 >99
3		30	>99	 >99
4		30	>99	 >99
5[b]		24	>99	 >99
6[b]		24	>99	 >99
7[b]		24	>99	 >99
8[b]		60	95	 >99
9		34	>99	 >99
10		40	>99	 >99
11		45	>99	 >99
12		40	>99	 >99
13[b]		45	>99	 >99
14[b]		35	>99	 >99
15[b]		35	>99	 >99
16[b]		36	>99	 93
17		30	>99	 >99
18[c]		50	>99	 >99
19[c]		46	>99	 >99
20[b,c]		40	>99	 90
21[b,c]		46	>99	 >99
22[b,c]		24	>99	 90
23[d]		80	80	 >99
24[b]		50	>99	 >99
25[b]		50	>99	 >99
26[d]		60	95	 >99
27[d]		50	98	 >99
28		20	>99	 >99
29		20	>99	 >99

[a] Reaction conditions: substrate (0.5 mmol), Co@C-N-900-15h (Co 10 mol%), isopropanol(2 mL), 80 ℃. [b] 100 ℃. [c] Isopropanol (1 mL). [d] Catalyst (Co 20 mol%), 150 ℃.

As compared to traditional pathway of nitriles hydrogenation (high molecular hydrogen pressures, ca. 1-5 MPa),[12] transfer hydrogenation represents an attractive route to amines owing to the relatively mild reaction conditions which avoided the use of any high pressure equipment.[2] However, the transfer hydrogenation of nitriles is particularly difficult because of easy formation of the corresponding methyl group.[13] Particularly for aliphatic nitriles (e.g.*n*-pentanenitrile and phenylacetonitrile), moderate yields or even no corresponding products could be detected.[14] Nevertheless, *m*-tolunitrile, *o*-tolunitrile, 1-naphthonitrile, and even aliphatic nitriles smoothly underwent transfer hydrogenation under mild reaction conditions, with yields over 90% for the desired products (Table 1, entries 18-22).

Transfer hydrogenation also provides an excellent method for the hydrogenation of nitro compounds as compared to hydrogenations using molecular hydrogen under high pressure.[15] In the present catalytic system, the transfer hydrogenation of nitrobenzene and derivates with isopropanol were conducted at ambient pressure at 120-150 ℃, giving the corresponding amines in good to excellent yields (Table 1, entries 23-25). Transfer hydrogenation of halogenated nitrobenzene was more challenging due to dehalogenation.[16] However, in our system the reactions of halogenated nitrobenzenes such as p-chloronitrobenzene and p-iodonitrobenzene were found to be promoted under the investigated reaction conditions to afford the desired products in excellent yields with >99% selectivity (Table 1, entries 26-27).

Furthermore, we also investigated the transfer hydrogenation of C=C bonds. Excellent conversions and selectivities were obtained for cycloalkenes without the detection of ring opening by-products under the investigated conditions (Table 1, entries 28-29). The reaction results summarized in Table 1 demonstrated the general applicability of this catalytic system in the transfer hydrogenation of various unsaturated chemicals including aldehydes, ketones, nitro-compounds, nitriles, and alkenes.

Two different reaction mechanisms have been proposed for the transfer hydrogenation in the presence of base additives.[17] Similarly, both of them suggest that the presence of bases may facilitate the formation of metal hydrides for the transition-metal catalyzed

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transfer hydrogenation reactions.[18] As demonstrated by CO_2-TPD (Fig. 5), basic sites were present in as-synthesized Co@C-N materials. Therefore, we speculated that the basic sites on Co@C-N might play a similar role to that of base additives to facilitate the transfer of protons to Co nanoparticles to form Co metal hydride species, thus promoting the production of the desired hydrogenation products.

In summary, we have developed a novel non-noble Co@C-N system for catalytic transfer hydrogenation reactions. The heterogeneous Co@C-N catalysts, prepared using a Co-containing MOF as sacrificial template, were proved to be highly active and selective in the hydrogenation of a variety of unsaturated bonds with isopropanol in the absence of any base additives. Moreover, the catalysts are magnetically separable (Fig. S11) and reusable under the investigated conditions. The combination of high efficiency, versatility and recyclability as well as mild reaction conditions (in the absence of bases and gaseous hydrogen) makes this system an attractive alternative pathway for various hydrogenation processes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, catalysts characterization, and additional reaction results. See DOI: 10.1039/c000000x/

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