EDGE ARTICLE

Reusable Co-nanoparticles for general and selective *N*-alkylation of amines and ammonia with alcohols†

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A general cobalt-catalyzed *N*-alkylation of amines with alcohols by borrowing hydrogen methodology to prepare different kinds of amines is reported. The optimal catalyst for this transformation is prepared by pyrolysis of a specific templated material, which is generated *in situ* by mixing cobalt salts, nitrogen ligands and colloidal silica, and subsequent removal of silica. Applying this novel Co-nanoparticle-based material, >100 primary, secondary, and tertiary amines including *N*-methylamines and selected drug molecules were conveniently prepared starting from inexpensive and easily accessible alcohols and amines or ammonia.
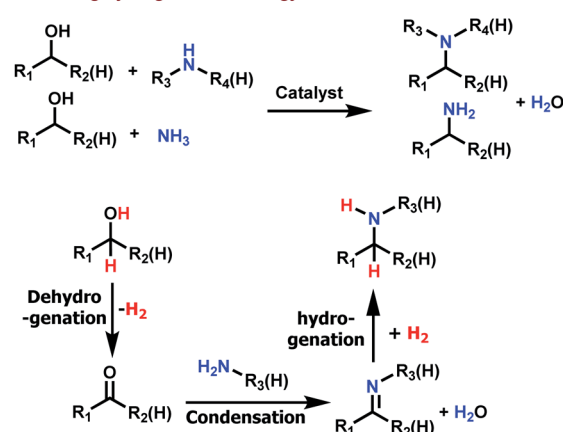
Introduction

In organic synthesis, carbon–nitrogen bond forming reactions represent a valuable synthetic toolbox, which allows direct access to all kinds of amines.[1–11] In general, amines are indispensable fine and bulk chemicals, widely used as precursors and intermediates for many daily life products.[3–5,12–14] In addition, amine/nitrogen moieties constitute integral parts of most drugs and biomolecules and play a key role for their activities.[13,14] Because of their importance a plethora of methods have been developed to create C–N bonds. Traditionally, stoichiometric nucleophilic substitution reactions and reductive aminations with (over)stoichiometric amounts of metal hydrides prevailed in this area.[3–5] In recent decades and today, the focus for C–N bond formation is more on catalytic methodologies due to improved selectivity control and waste minimization. Among these methods, alcohol aminations (*N*-alkylation with alcohols; Scheme 1)[8–12] as well as hydroaminations of olefins[6] are especially interesting due to their intrinsic atom efficiency. In particular, amination of alcohols *via* so-called borrowing hydrogen (BH) or hydrogen auto-transfer methodology[7–11] offers the following advantages: (a) utilization of alcohols as the

starting materials, which are inexpensive and easily accessible including bio-based feedstocks; (b) no need for any external/additional hydrogen as the alcohol itself serves as the hydrogen donor; and (c) high step- and atom-economy as water is the only by-product.

In Scheme 1, the generally accepted mechanism for amination of alcohols is shown: first the alcohol undergoes catalytic dehydrogenation to give the corresponding aldehyde (or ketone), which is then condensed with the amine to form the respective imine. Finally, this imine is hydrogenated to yield the desired amine product.

A variety of molecularly-defined catalysts have been successfully developed for catalytic *N*-alkylation of amines with

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Scheme 1 Borrowing hydrogen methodology for carbon–nitrogen bond formation from alcohols.

alcohols;[15–21] however, in recent years there is a special focus on 3d metal complexes.[16–21] While many of these homogeneous systems offer broad substrate scope and general applicability, their drawbacks are stability and difficult recycling. On the other hand, heterogeneous catalysts[22] for hydrogen borrowing reactions including supported Ni,[23–27] Fe-,[28] and Cu-based[27,29–32] systems are stable, but have been scarcely applied for advanced organic synthesis. Thus, the development of heterogeneous catalysts, which are stable, inexpensive and at the same time exhibit both generality and high selectivity for hydrogen barrowing reactions is still desirable.

In recent years, we and others have explored metal complexes with nitrogen-containing ligands and metal organic frameworks (MOFs) with different linkers as suitable precursors for the preparation of supported metal nanoparticles.[33–38] After controlled pyrolysis, well dispersed metal nitrogen carbon structures are formed. The resulting materials were successfully applied for many hydrogenation,[33] oxidation,[34] and reductive amination reactions.[35,36] However, to the best of our knowledge such materials have not been explored for N-alkylation of amines with alcohols. In this respect, herein we report novel supported cobalt-nanoparticles as a general hydrogen borrowing catalyst for the preparation of amines. The optimal nanocatalyst is prepared by pyrolysis of a templated material obtained *in situ* from cobalt–phenanthroline complex and commercially available colloidal silica (LUDOX® HS-40; 40 wt% suspension in H_2O) and subsequent removal of silica content. Aromatic, heterocyclic, and aliphatic secondary and tertiary amines can be conveniently and selectively prepared starting using various alcohols. Further, this novel catalyst is also active and selective for the amination of alcohols with ammonia.

Results and discussion

Preparation and catalytic evaluation of Co-nanoparticles

At the start of this project, we prepared several potential cobalt catalysts *via* co-precipitation of $Co(NO_3)_2 \cdot 6H_2O$ in the presence of di- and tri-dentate nitrogen ligands (1,10-phenanthroline (phen; L1), 2,2′-bipyridine (bpy; L2), 2,2′; 6′,2″-terpyridine (tpy; L3), 2,6-bis(2-benzimidazolyl)pyridine (bbp; L4)) and colloidal silica (LUDOX® HS-40; 40 wt% suspension in H_2O) (Fig. 1, steps 1 and 2). After pyrolysis of the templated material containing cobalt–nitrogen complexes on silica under argon at 800 °C (Fig. 1, step 3), the residual silica was removed *via* treatment with ammonium hydrogen fluoride (NH_4HF_2) (Fig. 1, step 4). The details of the synthetic procedure are described in SI. The resulting cobalt materials are represented as Co@NC-T-L, where T and L denotes pyrolysis temperature and ligand, respectively.

The activities and selectivities of these Co-materials (Co@NC-T-L) were initially evaluated for the N-alkylation of aniline 1 with benzyl alcohol 2 to prepare N-benzylaniline 3 in presence of 1 equivalent of t-BuOK at 140 °C for 24 h in toluene (Fig. 2; Table S1†). Under these conditions all the prepared catalysts from different Co–nitrogen complexes showed good to excellent activities and selectivities for the benchmark reaction (Fig. 2; Table S1,† entries 1–4). Among the prepared materials, Co@NC-800-L1 was found to be the best and quantitative yield
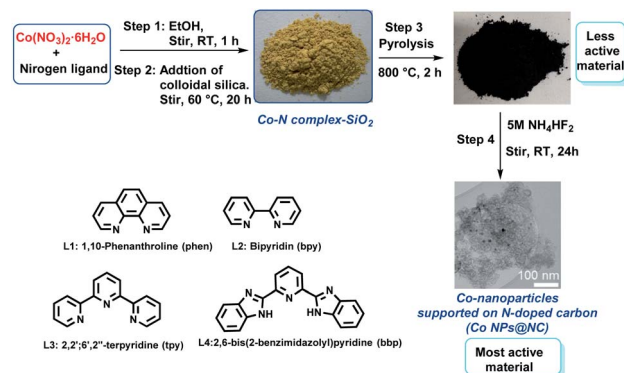

Fig. 1 Preparation of novel cobalt nanoparticles supported on N-doped carbon.
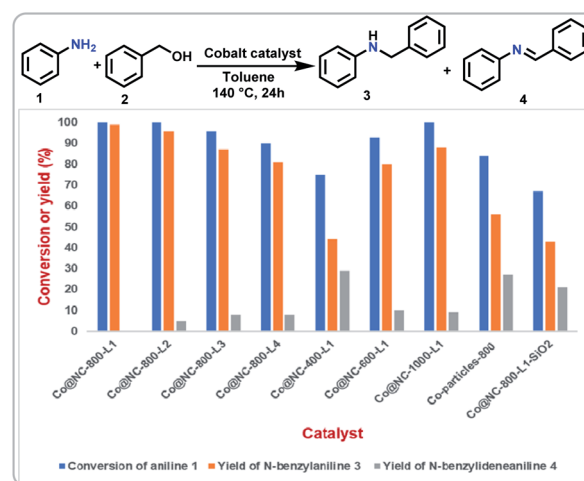

Fig. 2 N-Alkylation of aniline with benzyl alcohol: Testing of cobalt catalysts. Reaction conditions: 0.5 mmol aniline, 1 mmol benzyl alcohol, 15 mg catalyst (0.86 mol% Co), 0.5 mmol t-BuOK (1 equiv.), 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC using n-hexadecane standard.

of the desired product 3 was obtained (Fig. 2; Table S1,† entry 1). Comparing the materials prepared at different pyrolysis temperature (400–1000 °C) revealed 800 °C as the best one (Fig. 2; Table S1,† entries 1, 5–7).

The material prepared using the cobalt nitrate precursor, without any ligand, was found to be less active and produced 56% of the desired product (Fig. 2; Table S1,† entry 8). Similarly, the pyrolyzed material with silica (Co@NC-800-L1-SiO₂) exhibited lower activity and provided 43% yield of 3 (Fig. 2; Table S1,† entry 9). Applying Co@NC-800-L1, the model reaction is also promoted in the absence of base and gave 57% of N-benzylaniline 3 (Table S1,† entry 10), while without cobalt catalyst only minor amounts of 3 are formed (Table S1,† entry 11), which is in accordance with previous observations.[39,40] Further, different solvents, bases, and other reaction parameters such as temperature, amount of catalyst and reaction time were evaluated for the model reaction (Tables S2–S4†). Next, we compared the activity of our optimal catalyst with selected previously reported

catalysts for alcohol aminations. As shown in Table S5,† Co@NC-800-L1 worked more efficiently and required less amount of catalyst loading than the compared systems.

Characterization of Co-based materials

The optimal catalyst (Co@NC-800-L1) and a less active material (Co-particles-800; without ligand) as well as a recycled (Co@NC-800-L1-R) catalyst were characterized using X-ray powder diffraction (XRD), scanning transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction pattern of the most active catalyst (Co@NC-800-L1) showed peaks at $2\theta = 44.40°$ and $2\theta = 51.6°$, which are assigned to metallic cobalt nanoparticles of fcc cobalt (JCPDS 15-0806) and hcp cobalt (JCPDS 05-0727)[41] (Fig. S1†). The broad peak observed in the range of $2\theta = 20$–$30.8°$ belongs to reflections of graphitized carbon (Fig. S1†). In the XRD of the recycled catalyst sample, Co@NC-800-L1-R, identical cobalt species similar to the fresh catalyst are detected. In the less active sample (Co-particles-800), which was prepared without any ligand, the formation of cobalt silicate phases is observed (Fig. S2†).

TEM analysis of Co@NC-800-L1 showed the formation of small cobalt nanoparticles with a spherical morphology and the size up to ~12 nm (Fig. 3–c). Further, HAADF-STEM (Fig. 3d) and elemental mapping (Fig. 3e–j) confirmed that Co-nanoparticles are dispersed uniformly on N-doped carbon sheets. The existence of a small quantity of Si might be resulted from silica precursor, which was used during catalyst preparation.

According to TEM images of the recycled catalyst, nanoparticle size and shape of cobalt species remained intact inside the framework (Fig. S4†), while images of the less active sample (Co-particles-800; prepared without ligand) displayed the cobalt species anchored and distributed over the remaining silica surface (Fig. S5†).

The chemical composition at the surface of the most active catalyst, Co@NC-800-L1 was investigated by X-ray photoelectron spectroscopy. In the C 1s spectra, five peaks are observed
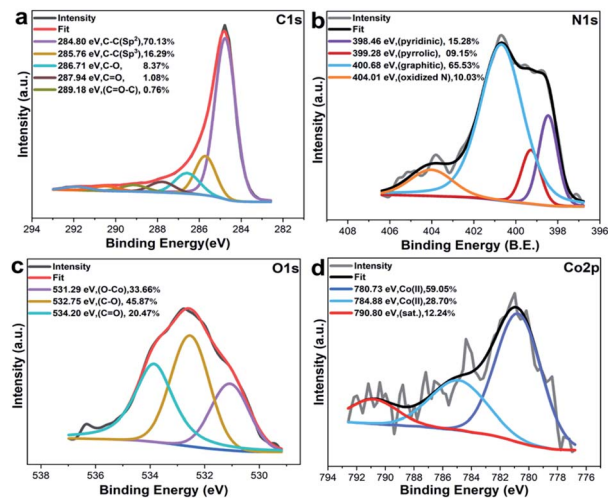

Fig. 4 High resolution X-ray photoelectron spectra (HR-XPS) for Co@NC-800-L1. (a) C 1s, (b) N 1s, (c) O 1s, and (d) Co 2p region.

(Fig. 4a). Two peaks at ~284.8, and ~285.76 eV are assigned for the sp^2-hybridized graphite-like carbon and the sp^3-hybridized carbon. The other three peaks at ~286.71, ~287.94 and 289.18 eV are associated to the surface oxygen groups including C–O, C=O and C=O–C, respectively.[42]

The N 1s spectra (Fig. 4b) displayed four peaks fitted with binding energies at 398.46, 399.28, 400.68 and 404.01 eV corresponding to pyridinic, pyrrolic, graphitic and oxidized N atoms, respectively.[43] The O1s spectra (Fig. 4c) contributed three peaks at 531.29, 532.75 and 534.20 eV, which correspond to Co–O bonds, C–O, and C=O bonds.[44] The binding energy at 532.75 eV is usually reported for partially hydrated oxides groups (such as –OH and –COOH) bonded with carbon.[45] In the cobalt region, Co $2p_{3/2}$ peaks located at 780.73 eV (50.05%) and 784.88 eV (28.70%) are attributed to Co(II) species[46] with 790.80 eV satellite peak (Fig. 4d). In the recycled catalyst, Co@NC-800-L1, identical cobalt species have been observed with similar binding energies and oxidation state like in the case of the fresh catalyst demonstrating the catalyst is highly stable (Fig. S6†).

Stability, recycling, and reusability of the Co@NC-800-L1 catalyst

For any given heterogeneous catalyst its stability and reusability are important aspects to allow for cost-efficient applications. To prove these features, we performed recycling experiments for the model reaction under two different reaction conditions (24 h, complete conversion and 5 h, around 60% conversion). As shown in Fig. 5, Co@NC-800-L1 exhibited high stability and was recycled and reused up to 7 times without significant deactivation.

N-Alkylation of aniline with different alcohols

With an optimal catalyst (Co@NC-800-L1) in hand, we explored its general applicability for the synthesis of primary, secondary, and tertiary amines including *N*-methylated products. First, we
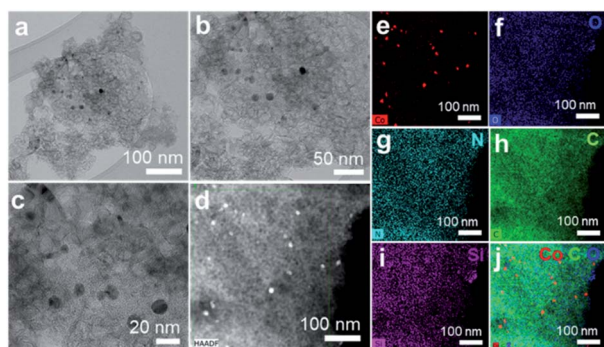

Fig. 3 a–c) TEM images of Co@NC-800-L1, (d) HAADF-STEM image, corresponding element maps showing the distribution of (e) cobalt (red), (f) oxygen (blue), (g) nitrogen (cyan), (h) carbon (green), (i) silica (purple) and (j) cobalt/carbon/oxygen together (red/green/blue).
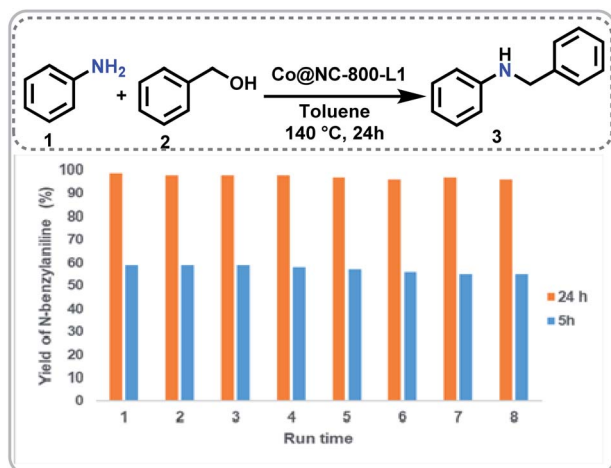
Fig. 5 Stability and recycling of Co@NC-800-L1 catalyst for the synthesis of *N*-benzylaniline. Reaction conditions: 1 mmol aniline, 2 mmol benzyl alcohol, 30 mg catalyst (0.86 mol% Co), 1 mmol *t*-BuOK, 3 mL toluene, 140 °C, 24 h and 5 h. Conversions and yields are based on aniline and determined by GC using *n*-hexadecane standard.

investigated the scope of alcohols for the *N*-alkylation of aniline. As shown in Scheme 2, various benzylic, heterocyclic, and aliphatic primary alcohols as well as secondary alcohols reacted well with aniline and gave the corresponding *N*-benzyl anilines in up to 87% yield (Scheme 2; products **5–14**). Ether-, thioether-, hydroxy-, nitrile-, nitro-, halide (F, Cl), and silyl-containing benzyl alcohols reacted smoothly and provided a variety of functionalized secondary amines (Scheme 2; products **15–23**). Next, different heterocyclic alcohols such as nicotinyl, furfuryl, and piperonyl alcohol, as well as 2-thiophenemethanol, tetra-hydroquinoline-, benzodioxine-, and morpholine-based alco-hols were coupled with aniline to provide the corresponding heterocyclic secondary amines in up to 89% yield (Scheme 2; products **24–31**). Notably, diamination of 2,6-pyr-idinedimethanol proceeded well and both alcohol groups reacted to give 87% of product **32**. Compared to benzylic alco-hols, aliphatic alcohols are less reactive and thus more difficult to aminate. Nevertheless, our catalyst allowed for amination of such substrates too, albeit at higher temperature in the pres-ence of 2.8 mol% catalyst (Scheme 2; products **33–40**). Under these conditions linear and cyclic aliphatic alcohols gave up to 87% of *N*-alkylated amines. In addition, allylic amines are selectively produced in up to 77% yield without significant hydrogenation of the C–C double bond. Similar selectivity is observed for perillyl alcohol, a naturally occurring monoterpene derivative (Scheme 2; product **40**). Apart from primary alcohols, even more demanding reaction of secondary alcohols with aniline provided the corresponding amines in up to 84% yield (Scheme 2; products **41–46**). Such aminations are particularly challenging because the reduction of corresponding imine is more difficult. As an example, the amination of estrone, an important steroid derivative, gave the desired product in 60% yield (Scheme 2; product **47**).
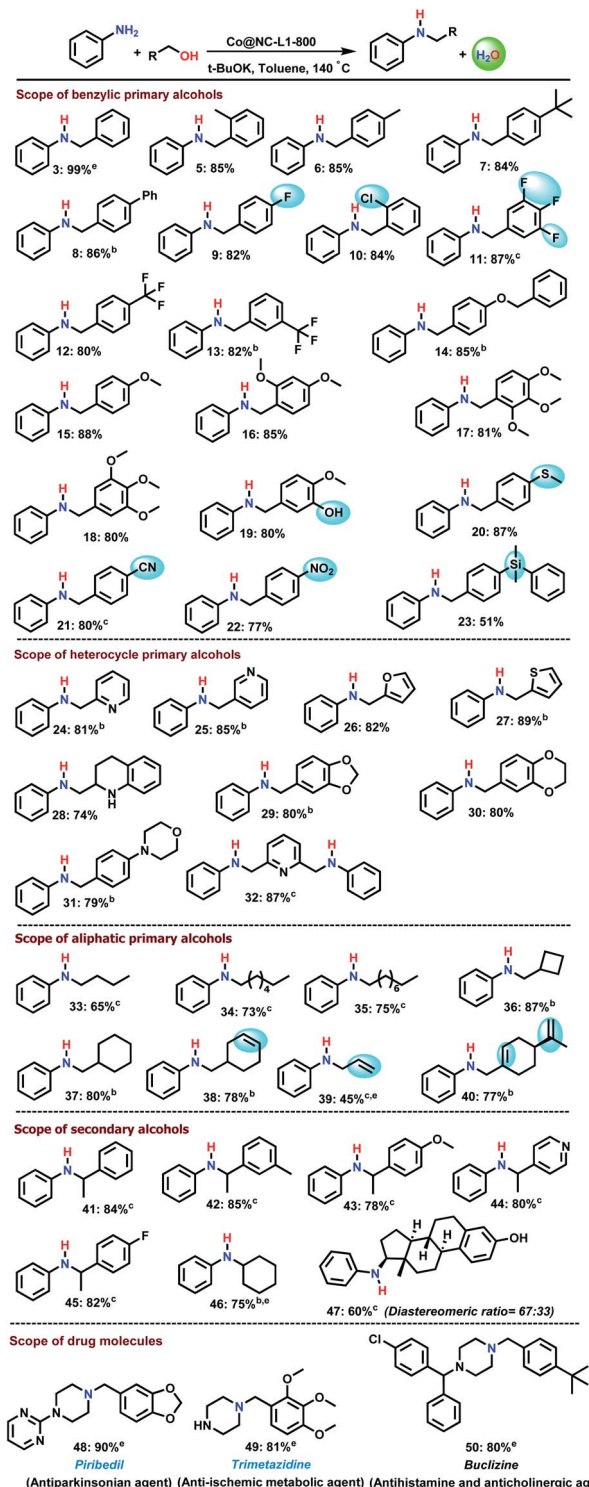

Scheme 2 Co-nanoparticles catalyzed *N*-alkylation of aniline with different alcohols[a]. [a] Reaction conditions: 0.5 mmol aniline, 1 mmol alcohol, 15 mg catalyst (0.86 mol% Co), 0.5 mmol *t*-BuOK (1 equiv.), 2 mL toluene, 140 °C, isolated yields. [b] same as "a" with 30 mg catalyst (1.7 mol% Co). [c] same as [a] with 50 mg catalyst (2.8 mol% Co) at 160 °C. [d] same as "c" at 150 °C. [e] GC yields.

Finally, the usefulness of this Co-based borrowing hydrogen methodology is showcased for the preparation of selected drug molecules, such as Piribedil, Trimetazidine, and Buclizine

(Scheme 2, products **48–50**). To prepare these molecules, piperazine and *N*-substituted piperazines were reacted with piperonyl alcohol, 2,3,4-trimethoxybenzyl alcohol and 4-*tert*-butyl benzyl alcohol under previously optimized conditions. In general, these and related drug molecules are prepared by reductive amination reactions using specific catalysts in presence of molecular hydrogen or sodium borohydride. In addition, certain products have been synthesized utilizing nucleophilic substitution reactions of corresponding amines and halogenated compounds. Advantageously, the here presented Co-catalysed BH-methodology does not require additional reducing agents and not produces any amount of halide waste.
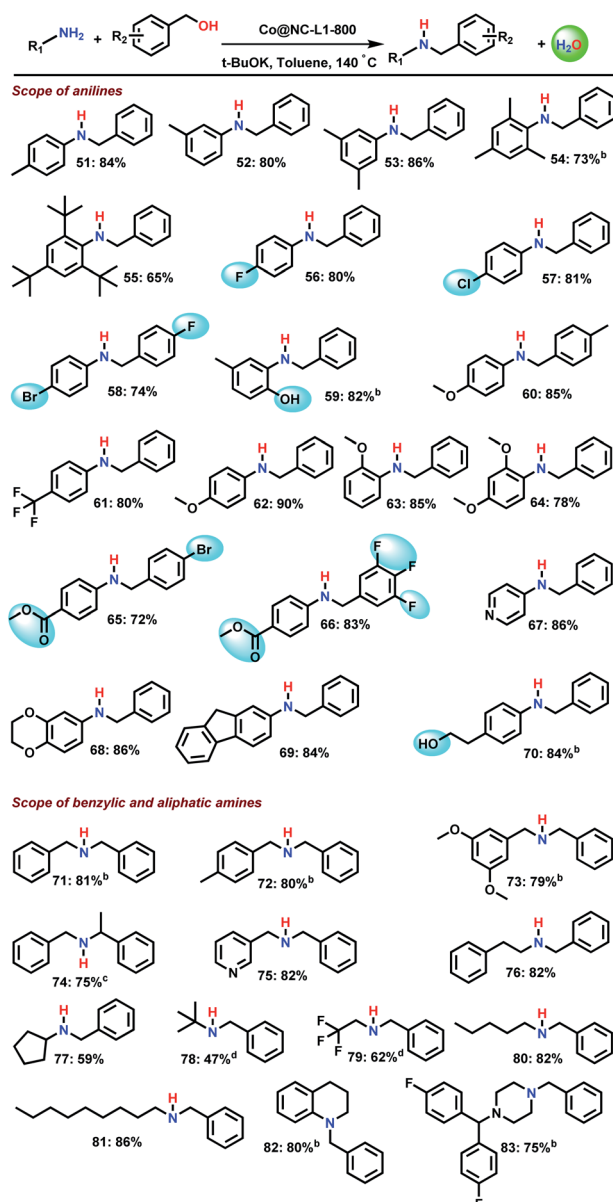
Scheme 3 *N*-Alkylation of different amines with benzyl alcohol using Co-nanoparticles[a]. [a] Reaction conditions: 0.5 mmol amine, 1 mmol alcohol, 0.5 mmol *t*-BuOK (1 equiv.), 2 mL toluene, 140 °C, 24 h, isolated yields. [b] same as "a" with 30 mg catalyst (1.7 mol% Co). [c] same as "a" with 50 mg catalyst (2.8 mol% Co) at 160 °C. [d] GC yields.
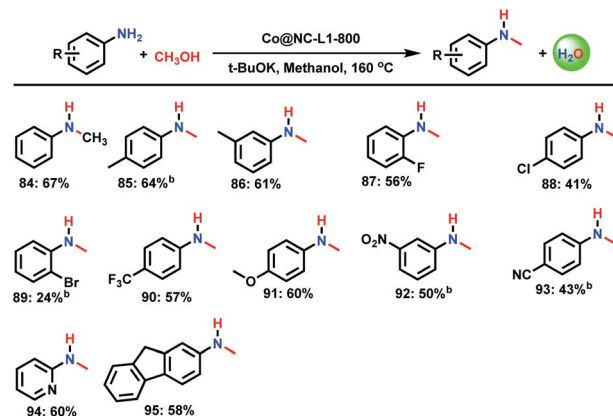
Scheme 4 Co-catalysed synthesis of *N*-methylamines using methanol[a]. [a] Reaction conditions: 0.5 mmol amine, 60 mg catalyst (3.5 mol% Co), 2 mL methanol, 1 mmol *t*-BuOK, 160 °C, 24 h, isolated yields. [b] GC yields.

## *N*-Alkylation of different amines with benzylic alcohols: scope of amines

Next, we explored the scope of amines and a series of substituted and functionalized *N*-benzylanilines was prepared including sterically hindered derivatives (Scheme 3, products **51–55**). In addition, F⁻, Cl⁻, Br-, and CF₃₋substituted as well as methoxy-, hydroxy-, and ester-containing substrates provided the corresponding products in up to 86% yield (Scheme 3; products **56–66**). Likewise, benzylic, araliphatic and aliphatic primary amines reacted well to give *N*-alkylated products in up to 82% (Scheme 3, products **71–81**). With respect to secondary amines, tetrahydroquinoline- and piperazine-based amines were *N*-benzylated smoothly to tertiary amines (Scheme 3, products **82** and **83**).

N-Methylation of amines using methanol

A special class of *N*-alkylamines are *N*-methylated products, which play a vital role as biologically active and pharmaceutically relevant compounds. Compared to traditional reagents such as methyl iodide and dimethyl sulfate, methanol constitutes a more benign methylation source, which is abundant, inexpensive and produces water as the only by-product. As shown in Scheme 4, Co@NC-800-L1 catalyst is also active and highly selective towards mono-*N*-methylation.

Synthesis of primary amines from alcohols and ammonia

The successful synthesis of secondary and tertiary amines inspired us to test the applicability of our Co-catalyst for the amination of alcohols with ammonia to obtain primary amines. In general, this reaction is difficult and often secondary or tertiary amines or mixtures are formed due to the higher reactivity of the *in situ*-formed primary amines compared to ammonia. Nevertheless, Co@NC-800-L1 catalysed the synthesis of primary amines using gaseous ammonia (Scheme 5). More specifically, 13 simple, halogenated, and functionalized
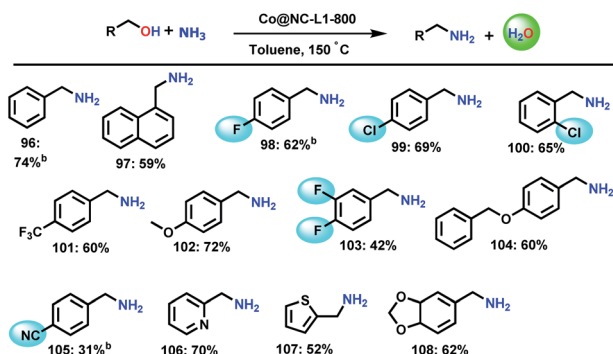
Scheme 5 Co-nanoparticles catalysed synthesis of primary amines from alcohols and ammonia[a]. [a] Reaction conditions: 0.5 mmol alcohol, 5–7 bar NH_3, 60 mg catalyst (3.5 mol% Co), 0.5 mmol t-BuOK, 2 mL toluene, 24 h, isolated yields. [b] GC yields.

benzylic as well as heterocyclic primary amines were prepared in up to 70% yield.

Conclusions

Here, we present a novel heterogeneous catalyst based on stable and reusable cobalt nanoparticles supported on N-doped carbon for the general and selective synthesis of amines from alcohols by borrowing hydrogen methodology. The optimal catalytic material is prepared by the pyrolysis of a Co–nitrogen complex-SiO_2 templated material, which is generated by mixing cobalt nitrate, 1,10-phenanthroline, and colloidal silica, and subsequent removal of the later. Applying these nanoparticles many functionalized and structurally diverse primary, secondary, and tertiary amines including N-methylamines and selected drug molecules can be conveniently prepared starting from inexpensive and easily available alcohols and amines or ammonia.

Data availability

All experimental data associated with this work is available in the ESI.†

Author contributions

RVJ and MB supervised the project. ZM, RVJ and MB planned and developed the project, and designed the experiments. ZM prepared and developed catalysts and performed all catalytic experiments. BZ and XL, co-performed catalytic experiments and reproduced the results. RGM, MBG, MP and RZ performed catalysts characterization. RVJ, ZM and MB wrote the paper. RGM, MBG, and RZ co-wrote the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 J. Bariwal and E. Van der Eycken, *Chem. Soc. Rev.*, 2013, **42**, 9283–9303.
2 P. Ruiz-Castillo and S. L. Buchwald, *Chem. Rev.*, 2016, **116**, 12564–12649.
3 T. Irrgang and R. Kempe, *Chem. Rev.*, 2020, **120**, 9583–9674.
4 K. Murugesan, T. Senthamarai, V. G. Chandrashekhar, K. Natte, P. C. Kamer, M. Beller and R. V. Jagadeesh, *Chem. Soc. Rev.*, 2020, **49**, 6273–6328.
5 O. I. Afanasyev, E. Kuchuk, D. L. Usanov and D. Chusov, *Chem. Rev.*, 2019, **119**, 11857–11911.
6 T. E. Muller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795–3892.
7 A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410–1459.
8 T. Irrgang and R. Kempe, *Chem. Rev.*, 2018, **119**, 2524–2549.
9 B. G. Reed-Berendt, D. E. Latham, M. B. Dambatta and L. C. Morrill, *ACS Cent. Sci.*, 2021, **7**, 570–585.
10 G. Guillena, D. J. Ramon and M. Yus, *Chem. Rev.*, 2010, **110**, 1611–1641.
11 F. Shi and X. Cui, *Catalytic amination for N-alkyl amine synthesis*, Elsevier., 2018.
12 S. A. Lawrence, *Amines: synthesis, properties and applications*, Cambridge University Press, 2004.
13 A. Ricci, *Amino group chemistry: from synthesis to the life sciences*, John Wiley & Sons., 2008.
14 https://njardarson.lab.arizona.edu/sites/njardarson.lab.arizona.edu/files/Top%20200%20Pharmaceuticals%20By%20Retail%20Sales%202020V3.pdfTop 200 Pharmaceuticals by Retail Sales in 2020.
15 (*a*) D. Pingen, C. Müller and D. Vogt, *Angew. Chem., Int. Ed.*, 2010, **49**, 8130–8133; (*b*) M. H. S. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. Watson and J. M. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 1766–

1774; (*c*) T. T. Dang, B. Ramalingam, S. P. Shan and A. M. Seayad, *ACS Catal.*, 2013, **3**, 2536–2540; (*d*) J. J. A. Celaje, X. Zhang, F. Zhang, L. Kam, J. R. Herron and T. J. Williams, *ACS Catal.*, 2017, **7**, 1136–1142; (*e*) B. Emayavaramban, P. Chakraborty, E. Manoury, R. Poli and B. Sundararaju, *Org. Chem. Front.*, 2019, **6**, 852–857; (*f*) C. Gunanathan and D. Milstein, *Angew. Chem.*, 2008, **120**, 8789–8792.

16 T. Yan, B. L. Feringa and K. Barta, *Nat. Commun.*, 2014, **5**, 1–7.

17 (*a*) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 1–8; (*b*) N. Deibl and R. Kempe, *Angew. Chem., Int. Ed.*, 2017, **56**, 1663–1666.

18 M. Vayer, S. P. Morcillo, J. Dupont, V. Gandon and C. Bour, *Angew. Chem., Int. Ed.*, 2018, **57**, 3228–3232.

19 A. Quintard, T. Constantieux and J. Rodriguez, *Angew. Chem., Int. Ed.*, 2013, **52**, 12883–12887.

20 N. Deibl and R. Kempe, *J. Am. Chem. Soc.*, 2016, **138**, 10786–10789.

21 (*a*) M. Vellakkaran, K. Singh and D. Banerjee, *ACS Catal.*, 2017, **7**, 8152–8158; (*b*) M. Subaramanian, S. P. Midya, P. M. Ramar and E. Balaraman, *Org. Lett.*, 2019, **21**, 8899–8903.

22 (*a*) A. S. Alshammari, K. Natte, N. V. Kalevaru, A. Bagabas and R. V. Jagadeesh, *J. Catal.*, 2020, **382**, 141–149; (*b*) A. Corma, T. Ródenas and M. J. Sabater, *Chem.–Eur. J.*, 2010, **16**, 254–260; (*c*) S. Rojas-Buzo, P. Concepción, A. Corma, M. Moliner and M. Boronat, *ACS Catal.*, 2021, **11**, 8049–8061.

23 (*a*) K.-i. Shimizu, S. Kanno, K. Kon, S. H. Siddiki, H. Tanaka and Y. Sakata, *Catal. Today*, 2014, **232**, 134–138; (*b*) K.-i. Shimizu, N. Imaiida, K. Kon, S. Hakim Siddiki and A. Satsuma, *ACS Catal.*, 2013, **3**, 998–1005.

24 K.-i. Shimizu, K. Kon, W. Onodera, H. Yamazaki and J. N. Kondo, *ACS Catal.*, 2013, **3**, 112–117.

25 A. Tomer, F. Wyrwalski, C. Przybylski, J.-F. Paul, E. Monflier, M. Pera-Titus and A. Ponchel, *J. Catal.*, 2017, **356**, 111–124.

26 A. Afanasenko, S. Elangovan, M. C. Stuart, G. Bonura, F. Frusteri and K. Barta, *Catal. Sci. Technol.*, 2018, **8**, 5498–5505.

27 X. Cui, X. Dai, Y. Deng and F. Shi, *Chem.–Eur. J.*, 2013, **19**, 3665–3675.

28 C. Gonzalez-Arellano, K. Yoshida, R. Luque and P. L. Gai, *Green Chem.*, 2010, **12**, 1281–1287.

29 F. Santoro, R. Psaro, N. Ravasio and F. Zaccheria, *ChemCatChem*, 2012, **4**, 1249–1254.

30 M. Dixit, M. Mishra, P. A. Joshi and D. O. Shah, *Catal. Commun.*, 2013, **33**, 80–83.

31 H. Liu, G.-K. Chuah and S. Jaenicke, *J. Catal.*, 2015, **329**, 262–268.

32 (*a*) Y. Wu, Y. Huang, X. Dai and F. Shi, *ChemSusChem*, 2019, **12**, 3185–3191; (*b*) S. Pang, Y. Deng and F. Shi, *ChemComm*, 2015, **51**, 9471–9474.

33 R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner and M. Beller, *Science*, 2013, **342**, 1073–1076.

34 R. V. Jagadeesh, T. Stemmler, A.-E. Surkus, M. Bauer, M.-M. Pohl, J. Radnik, K. Junge, H. Junge, A. Brückner and M. Beller, *Nat. Protoc.*, 2015, **10**, 916–926.

35 R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M.-M. Pohl, J. Radnik and M. Beller, *Science*, 2017, **358**, 326–332.

36 G. Hahn, P. Kunnas, N. de Jonge and R. Kempe, *Nat. Catal.*, 2019, **2**, 71–77.

37 K. Shen, X. Chen, J. Chen and Y. Li, *ACS Catal.*, 2016, **6**, 5887–5903.

38 N. Yan, Y. Yuan and P. J. Dyson, *Dalton Trans.*, 2013, **42**, 13294–13304.

39 F. Kallmeier, R. Fertig, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2020, **59**, 11789–11793.

40 S. Rösler, M. Ertl, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2015, **54**, 15046–15050.

41 R. Liu, Y. Zhao, R. Huang, Y. Zhao and H. Zhou, *CrystEngComm*, 2010, **12**, 4091–4094.

42 H. Wu, J. Geng, H. Ge, Z. Guo, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2016, **6**, 1600794.

43 Z. Du, X. Chen, W. Hu, C. Chuang, S. Xie, A. Hu, W. Yan, X. Kong, X. Wu and H. Ji, *J. Am. Chem. Soc.*, 2019, **141**, 3977–3985.

44 T. Choudhury, S. Saied, J. Sullivan and A. Abbot, *J. Phys. D: Appl. Phys.*, 1989, **22**, 1185–1195.

45 J. Li, S. Xiong, X. Li and Y. Qian, *J. Mater. Chem.*, 2012, **22**, 23254–23259.

46 Z. Wang, S. Peng, Y. Hu, L. Li, T. Yan, G. Yang, D. Ji, M. Srinivasan, Z. Pan and S. Ramakrishna, *J. Mater. Chem. A.*, 2017, **5**, 4949–4961.