nature portfolio

Peer Review File

A Universal Atomically Dispersed Cobalt Catalyst for the Efficient Alkylation of Ketones, Alcohols and Lignin-derived Compounds

Corresponding Author: Professor Matthias Beller

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This work presents the design and application of a novel heterogeneous cobalt single-atom catalyst (Co@NC-800-PPDA) for the C-alkylation of ketones, alcohols, and lignin-derived model compounds via a borrowing hydrogen (BH) strategy. The catalyst is synthesized through pyrolysis of a cobalt-poly(p-phenylenediamine) complex supported on silica, followed by silica removal, resulting in atomically dispersed Co–N_4 sites embedded in a mesoporous N-doped carbon matrix. Comprehensive characterization (XAFS, HAADF-STEM, XPS, etc.) confirms the atomic dispersion and local coordination of cobalt. The catalyst demonstrates exceptional activity, selectivity, and stability across a wide range of substrates, including functionalized and biomass-derived molecules, and enables C-methylation using methanol. Its utility is further highlighted in the valorization of KA oil and the synthesis of pharmaceutical intermediates. Overall, this work represents a notable contribution to green chemistry and atom-efficient C–C coupling. Hence, I recommend publication of this manuscript in " Nature Communications" after addressing the following points:

1. Despite the catalyst maintaining good stability after six cycles, ICP analysis on the cobalt content in the reaction solution after each cycle were not provided ? It is recommended to supplement relevant data to verify the absence of significant leaching during multiple cycles.

2. As indicated in Fig. 3, the material prepared from p-phenylenediamine demonstrates enhanced activity over that synthesized from aniline, despite both employing nitrogen species as metal anchoring sites. What accounts for the higher activity of the p-phenylenediamine-derived material?"

3. The Co-N_4 moiety is proposed as the primary active center in this study. It is suggested that a KSCN poisoning experiment for the model reaction be supplemented to further verify that the isolated Co-N_4 sites are indeed the dominant active centers, rather than potential Co nanoparticles or clusters that might contribute to the activity.

4. In Scheme 1, the product yields exhibit considerable variation (e.g., compounds 22-29). It is recommended to provide an explanation for the notably lower reactivity observed with aliphatic alcohols compared to their benzylic and heterocyclic counterparts.

5. The currently proposed reaction pathway is based on intermediate detection and control experiments. Isotopic labelling experiments, for instance using D-labelled alcohols, should be conducted to definitively confirm the hydrogen transfer pathway.

6. At Line 330, it is noted that "aliphatic ahools" is misspelled and it should be corrected to "aliphatic alcohols".

Reviewer #2

(Remarks to the Author)
Ma, Beller, and co-workers report the development of an atomically dispersed cobalt catalyst for borrowing-hydrogen-mediated C–C bond formation, addressing an important challenge at the interface of heterogeneous catalysis, organic synthesis, and biomass valorization. The authors prepare a mesoporous N-doped carbon-supported cobalt single-atom catalyst (Co@NC-800-PPDA) featuring Co-N4 coordination motifs, via a polymerization, assembly, template sacrificial strategy. Systematic investigations were conducted to evaluate the catalyst's catalytic performance in the C-alkylation of ketones, alcohols, lignin-derived compounds, and KA oil, confirming its superior activity, robust stability, excellent reusability, and broad substrate scope. Furthermore, this catalyst enables efficient methylation reactions using methanol as a C1 feedstock, thereby offering an alternative pathway for sustainable catalytic synthesis and the valorization of biomass resources. Overall, this work meets the academic standards and interdisciplinary impact criteria of Nature Communications. Addressing the following points would improve the impact of this work:
1. In the Introduction, the statement that nitrogen-based polymers such as PPDA or PANI have been “scarcely used” to generate metal–N centers is not sufficiently precise. Given the extensive use of PANI-derived N-doped carbons in Metal–N–C and electrocatalysis fields, the authors should revise this description to better delimit the specific context of borrowing-hydrogen C–C coupling or well-defined Co–N4 site construction.
2. The authors should provide quantitative turnover frequency (TOF) or site-normalized activity metrics. Given the emphasis on single-atom Co–N4 sites as the active centers, reporting only yields and conversions is insufficient for evaluating intrinsic catalytic performance.
3. The cobalt loading is reported for Co@NC-800-PPDA; however, Co contents for the other catalysts used for comparison (e.g., Co@NC-800-PANI, different pyrolysis temperatures, or silica-containing samples) are not consistently presented. Without this information, it is difficult to disentangle structural effects from metal loading effects. These data should be provided and discussed.
4. Since the authors identify Co–N4 moieties as the catalytically active sites, a clearer discussion linking this coordination environment to the key elementary steps of the borrowing-hydrogen mechanism (e.g., alcohol dehydrogenation and hydrogen transfer) would further strengthen the structure–activity relationship.
5. A clearer comparison with state-of-the-art heterogeneous and single-atom catalysts reported for similar C-alkylation or Guerbet-type reactions is necessary. Such a comparison should go beyond reaction scope and include activity, temperature, catalyst loading, and recyclability to better contextualize the advantages and limitations of the present system.
6. In Page 9, the high-resolution Co 2p XPS spectrum is interpreted as containing only $Co2^{+}$ species, with Co $2p_{3/2}$ peaks at 780.43 and 782.63 eV and a satellite at 790.80 eV (Fig. 4e). However, the deconvoluted spectrum clearly suggests the presence of at least two cobalt oxidation states. The fitted components are more consistent with a mixed $Co2^{+}/Co3^{+}$ state rather than a single $Co2^{+}$ species. This assignment should be revisited and corrected.
7. Minor issues related to clarity and presentation remain and should be addressed, including ensuring that all abbreviations are defined upon first use and correcting typographical errors (e.g., “aliphatic ahools”).

Reviewer #3

(Remarks to the Author)
In this manuscript, the author demonstrated that a novel and effective heterogeneous Co@NC-800-PPDA catalyst via pyrolysis of poly(p-phenylenediamine) enables excellent performance for borrowing hydrogen C-alkylation of ketones, alcohols, and lignin-derived feedstocks. The C-alkylation of lignin-derived feedstocks using alcohols as alkyl source is green and sustainable relative to halogenated compounds or organometallic reagents, so this work is of great significance. Compared to the previous reports, this synthetic protocol development of novel and effective Co@NC-800-PPDA catalyst which can be reused 6 times without obvious deactivation. A series of alcohol, and lignin-derived feedstocks were suitable for this heterogeneous cobalt SAC. Thus, I strongly recommend to publish it in the journal of Nat. Commun. after solving the following questions:
1. the authors reported a Co@NC-800-PPDA catalyst via pyrolysis of poly(p-phenylenediamine), explain the reasons for the use of the poly(p-phenylenediamine) as C and N sources for the Co@NC-800-PPDA catalyst. Have you tried other catalytic systems? it will inspire the reader on how to design new catalytic material for the reaction.
2. Supplementary Table 6, SI, KOMe (WM=70) shows a better performance than K3PO4 (WM=212), and 93% 3 and 95% 5 obtained. In the view of the mass ration of base to raw, KOMe is favorable. Why chose K3PO4 as the optimized base for the reaction?
3. In the reaction of Figure 3, 2.0 equiv. furfuryl alcohol was used, one equiv. furfuryl alcohol was converted the target product. What are the finally products of another other equiv. furfuryl alcohol? Do you observe the over-alkylation by-products via over-C-allylation of 2 with the product 3, or etherification by-product via reaction of obtained phenol 5 with furfuryl alcohol 2?
4. The base additive K3PO4 is important for the reaction, and the performance of the Co@NC-800-PPDA catalyst observed decreased (Supplementary Table 7, entry 1), can you explore the role of K3PO4.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
All concerns raised previously have been thoroughly addressed by the author, and it is recommended that the manuscript be accepted directly for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)
I have reviewed the revised manuscript and the authors' response to my comments. The authors have addressed all of my concerns through thoughtful revisions and additional discussions. I am now satisfied that the work is suitable for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)
Thanks for taking into consideration all our criticisms, recommendations, and questions.

Reply to the comments of Reviewers

Reply to the comments of Reviewer-1

This work presents the design and application of a novel heterogeneous cobalt single-atom catalyst (Co@NC-800-PPDA) for the C-alkylation of ketones, alcohols, and lignin-derived model compounds via a borrowing hydrogen (BH) strategy. The catalyst is synthesized through pyrolysis of a cobalt-poly(p-phenylenediamine) complex supported on silica, followed by silica removal, resulting in atomically dispersed Co-N_4 sites embedded in a mesoporous N-doped carbon matrix. Comprehensive characterization (XAFS, HAADF-STEM, XPS, etc.) confirms the atomic dispersion and local coordination of cobalt. The catalyst demonstrates exceptional activity, selectivity, and stability across a wide range of substrates, including functionalized and biomass-derived molecules, and enables C-methylation using methanol. Its utility is further highlighted in the valorization of KA oil and the synthesis of pharmaceutical intermediates. Overall, this work represents a notable contribution to green chemistry and atom-efficient C–C coupling. **Hence, I recommend publication of this manuscript in "Nature Communications" after addressing the following points:**

Reply: We thank the Reviewer for the positive assessment of our work, recognizing its contribution to green chemistry and atom-efficient C–C coupling, and for recommending publication in Nature Communications.

1. Despite the catalyst maintaining good stability after six cycles, ICP analysis on the cobalt content in the reaction solution after each cycle were not provided？ It is recommended to supplement relevant data to verify the absence of significant leaching during multiple cycles.

Reply: We thank the Reviewer for this valuable suggestion. As requested, we have performed ICP-OES analysis of both the reaction solutions and the recovered catalyst after each of the six recycling experiments. These data are now provided in the revised Supporting Information (Supplementary Table 12). The results show that the cobalt content in the recycled catalyst remained essentially identical to the fresh sample (1.24 wt% vs. 1.16 wt% after 6 cycles), and no cobalt species were detected in the reaction solutions. Combined with our hot-filtration test (Fig. 5), this confirms the truly heterogeneous nature and high stability of the catalyst.

Supplementary Table 12. ICP-OES analysis of both the reaction solution and recovered cobalt catalyst after each recycling experiment.

Recycle time	Co content in recovered material	Co content in reaction solution
fresh	1.24 wt%	-
1	1.22 wt%	-
2	1.21 wt%	-
3	1.20 wt%	-
4	1.18 wt%	-
5	1.16 wt%	-

2. As indicated in Fig. 3, the material prepared from p-phenylenediamine demonstrates enhanced activity over that synthesized from aniline, despite both employing nitrogen species as metal anchoring sites. What accounts for the higher activity of the p-phenylenediamine-derived material?"

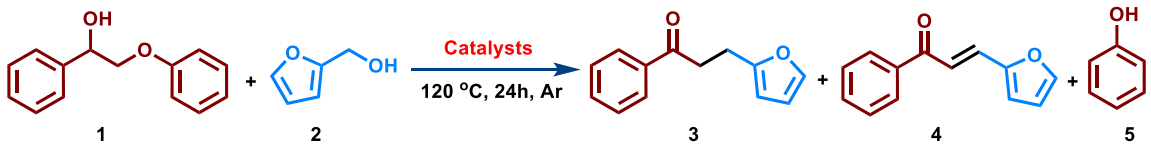
Reply: We appreciate this insightful question. While both precursors provide nitrogen anchoring sites, p-phenylenediamine (PPDA) features two amino groups in the para-position. This structure allows for a higher density of nitrogen coordination sites during polymerization and facilitates stronger, more symmetric chelation with cobalt precursors. Consequently, the PPDA-derived material generates more stable and abundant Co-N_4 active centers after pyrolysis compared to aniline, which only possesses a single amino group.

3. The Co-N_4 moiety is proposed as the primary active center in this study. It is suggested that a KSCN poisoning experiment for the model reaction be supplemented to further verify that the isolated Co-N_4 sites are indeed the dominant active centers, rather than potential Co nanoparticles or clusters that might contribute to the activity.

Reply: We have conducted the benchmark reaction in the presence of KSCN, a known selective poisoning agent for metal-N coordination sites. As shown in the revised SI (Supplementary Table 4, entry 6), the addition of KSCN led to a dramatic decrease in conversion (from >99% to <10%). This

sharp inhibition strongly substantiates that isolated Co-N_4 moieties are indeed the dominant active centers.

Supplementary Table 4. C-Alkylation of 2-phenoxy-1-phenylethanol with furfuryl alcohol: Effect of KSCN.[a]



Entry	Catalysts	Conv.1 (%)	Yield of 3 (%)	Yield of 4 (%)	Yield of 5 (%)
5	Co@NC-800-PPDA	>99	85	8	94
6[b]	Co@NC-800-PPDA + KSCN	<10	<5	<5	<10

Reaction conditions[a]: 0.3 mmol 2-phenoxy-1-phenylethanol, 0.6 mmol furfuryl alcohol, 40 mg catalyst, 0.18 mmol K_3PO_4 (0.6 equiv. based on **1**), 2 mL t-BuOH, 120 °C, 24 h, Ar. [b]: Poisoning experiment same as "a" with 40 mg Co@NC-800-PPDA and 0.3 mmol KSCN (30 mg). Conversions and yields were determined by GC using n-hexadecane standard based on **1**.

4. In Scheme 1, the product yields exhibit considerable variation (e.g., compounds 22-29). It is recommended to provide an explanation for the notably lower reactivity observed with aliphatic alcohols compared to their benzylic and heterocyclic counterparts.

Reply: We agree with the Reviewer's observation. The lower reactivity of aliphatic alcohols is attributed to the more difficult dehydrogenation step, which is the rate-determining stage in the Borrowing Hydrogen (BH) process. Benzylic and heterocyclic alcohols benefit from resonance stabilization of intermediates. We have added this explanation and cited relevant literature (*Angew. Chem. Int. Ed.* 2015, **54**, 14483-14486; *ACS Catal*. 2018, **8**, 10300-10305; *Chem. Sci*., 2022, **13**, 111-117) to support this interpretation in the revised manuscript.

5. The currently proposed reaction pathway is based on intermediate detection and control experiments. Isotopic labelling experiments, for instance using D-labelled alcohols, should be conducted to definitively confirm the hydrogen transfer pathway.

Reply: We thank the Reviewer for the suggestion. While isotopic labeling (e.g., with D-labeled alcohols) is powerful, we have not included new experiments because the BH mechanism for these types of transformations is already thoroughly established in literature for similar systems *Angew. Chem. Int. Ed.* 2020, **59**, 215-220). Their work using CD_3OD instead of MeOH reaction with 2-phenyl ethanol, led to deuterium incorporation in β- as well as α-position, supporting a BH mechanism. Furthermore, Wang (*Green Chem.*, 2020, **22**, 8452-8461) and Yi group (*Nano Res.* **15**, 1874-1881 (2022)) used $PhCD_2OH$ instead of $PhCH_2OH$ to verify the rate-determining step of the whole reaction, their results indicating that dehydrogenation of alcohol is the rate-determining step during the BH transformation. Thus, we have relied on intermediate detection and control experiments, which are consistent with the established BH pathway, and have added the respective literature citations to the mechanistic discussion.

6. At Line 330, it is noted that "aliphatic ahools" is misspelled and it should be corrected to "aliphatic alcohols".

Reply: We thank the Reviewer for pointing out this typo. The spelling has been corrected throughout the manuscript.

Reply to the comments of Reviewer-2

Ma, Beller, and co-workers report the development of an atomically dispersed cobalt catalyst for borrowing-hydrogen-mediated C–C bond formation, addressing an important challenge at the interface of heterogeneous catalysis, organic synthesis, and biomass valorization. The authors prepare a mesoporous N-doped carbon-supported cobalt single-atom catalyst (Co@NC-800-PPDA) featuring $Co-N_4$ coordination motifs, via a polymerization, assembly, template sacrificial strategy. Systematic investigations were conducted to evaluate the catalyst's catalytic performance in the C-alkylation of ketones, alcohols, lignin-derived compounds, and KA oil, confirming its superior activity, robust stability, excellent reusability, and broad substrate scope. Furthermore, this catalyst enables efficient methylation reactions using methanol as a C1 feedstock, thereby offering an alternative pathway for sustainable catalytic synthesis and the valorization of biomass resources. **Overall, this work meets the academic standards and interdisciplinary impact criteria of Nature Communications. Addressing the following points would improve the impact of this work:**

Reply: We thank the Reviewer highlighting the importance of our work and recognizing its interdisciplinary impact at the interface of heterogeneous catalysis, organic synthesis, and biomass valorization and his/her recommendation publishing this work in Nature Communications.

1. In the Introduction, the statement that nitrogen-based polymers such as PPDA or PANI have been "scarcely used" to generate metal–N centers is not sufficiently precise. Given the extensive use of PANI-derived N-doped carbons in Metal-N-C and electrocatalysis fields, the authors should revise this description to better delimit the specific context of borrowing-hydrogen C-C coupling or well-defined Co-N_4 site construction.

Reply: We acknowledge that PANI-derived carbons are widely used in electrocatalysis. Our intention was to highlight their rarity specifically in the context of BH-mediated C-C coupling. We have revised the Introduction to more precisely state: "Compared to mono- and diamine ligands, nitrogen-based polymers such as poly(p-phenylenediamine) (PPDA) and polyaniline (PANI) derived from p-phenylenediamine (PDA) and aniline (phenylamine: PA) respectively, have been rarely employed for the construction of well-defined Co-N_x coordination sites on supports, particularly in the context of BH coupling catalysis."

2. The authors should provide quantitative turnover frequency (TOF) or site-normalized activity metrics. Given the emphasis on single-atom Co-N_4 sites as the active centers, reporting only yields and conversions is insufficient for evaluating intrinsic catalytic performance.

Reply: As suggested by the Reviewer, we provided the TOF values of different Co-catalysts under standard reaction conditions in the revised manuscript. The TOF values of Co@NC-800-PPDA, Co@NC-800-PANI, Co@NC-400-PPDA, Co@NC-600-PPDA, Co@NC-1000-PPDA, Co-NPs-800, Co@NC-SiO_2-800-PPDA are 143, 132, 52, 107, 132, 41, 23, respectively. These results clearly show that Co@NC-800-PPDA catalyst exhibits a higher TOF than the other tested systems, demonstrating that the isolated Co-N_4 sites possess excellent intrinsic activity.

3. The cobalt loading is reported for Co@NC-800-PPDA; however, Co contents for the other catalysts used for comparison (e.g., Co@NC-800-PANI, different pyrolysis temperatures, or silica-containing samples) are not consistently presented. Without this information, it is difficult to disentangle structural effects from metal loading effects. These data should be provided and discussed.

Reply: We conducted ICP-OES analysis for all comparison samples. The loadings are now reported in the revised SI (Section S2). Most catalysts exhibit similar loadings (~1.2 wt%), confirming that the observed differences in activity are primarily due to structural and coordination effects. Elemental analysis of the optimal catalyst, Co@NC-800-PPDA: C = 64 wt.%, N = 8.5 wt.%, H = 0.72 wt.%, Si = 0.30 wt.%. The cobalt content was measured by ICP-OES to be approximately 1.24 wt.%. Furthermore,

the cobalt contents for Co@NC-800-PANI, Co@NC-400-PPDA, Co@NC-600-PPDA, Co@NC-1000-PPDA, Co-NPs-800, Co@NC-SiO_2-800-PPDA are 1.22, 1.45, 1.34, 1.17, 2.12, 1.86 wt%, respectively. These results confirm that the cobalt loadings across the different samples are relatively similar, except for the nanoparticle and silica-containing systems, and therefore the observed variations in catalytic performance can be primarily attributed to structural and coordination effects rather than differences in metal content. We have now included these data and the corresponding discussion in the revised manuscript to provide a clearer basis for comparison.

4. Since the authors identify Co-N_4 moieties as the catalytically active sites, a clearer discussion linking this coordination environment to the key elementary steps of the borrowing-hydrogen mechanism (e.g., alcohol dehydrogenation and hydrogen transfer) would further strengthen the structure-activity relationship.

Reply: We thank the Reviewer for this suggestion to strengthen the structure-activity relationship. We have expanded the discussion to explain how the well-defined electronic environment of Co-N_4 sites facilitates alcohol dehydrogenation by stabilizing transient hydride species and promotes efficient hydrogen transfer during the condensation/hydrogenation steps.

5. A clearer comparison with state-of-the-art heterogeneous and single-atom catalysts reported for similar C-alkylation or Guerbet-type reactions is necessary. Such a comparison should go beyond reaction scope and include activity, temperature, catalyst loading, and recyclability to better contextualize the advantages and limitations of the present system.

Reply: We agree that a broader contextualization is beneficial. Thus, we have added a comprehensive comparison table (Supplementary Table 11) in the SI, comparing our system with reported Pd, Ni, Fe, Cu, and Mn catalysts in terms of metal loading, temperature, and recyclability. Our system stands out as the first to successfully alkylate lignin-derived compounds via the BH-strategy.

Supplementary Table 11. State-of-the-art for the C-alkylation via BH-strategy with heterogeneous materials.

Entry	Catalyst	T (° C)/ t (h)	Substrates	Yield	Recycle times	Ref

1	SAC-Co (1.69 mol% Co)	120/6, 0.3 equiv. K_3PO_4	Ketones, alcohols and lignin derivates (>100 examples)	94%	6	This work
2	Pd/C (1.0 mol% Pd)	80/24, 1.5 equiv. K_3PO_4	Ketones (17 examples)	100%	4	4
3	Co-CIA	90/16, 1.0 equiv. $AgNTf_2$ and KF	Ketones, alcohols (32 examples)	93%	5	5
3	Pd/CeO_2-C (0.37 mol% Pd)	130/12, 0.25 equiv. K_3PO_4	Ketones (23 examples)	97%	3	6
4	MnO_2@PDCS (1.4mol% Mn)	120/12, 1.0 equiv. NaOH	Ketones, alcohols (57 examples)	89%	5	7
5	Mn@CeO_2 (3.64 mol%Mn)	130/12, 0.5 equiv. NaOH	Ketones (24 examples)	98%	6	8
6	Mn-MgO/Al_2O_3 (9.1 mol% Mn)	160/6	Ketones (16 examples)	95%	3	9
7	Cu/CuOx-250 (> 60 mol% Cu)	170/6 h, 0.5 equiv. K_3PO_4	Ketones (24 examples)	92%	3	10
8	Cu-HT (3.0 wt% Cu)	180/15	Ketones (9 examples)	80%	-	11
9	LCN@Zn-SAC (1.5 mol% Zn)	110/4, 0.3 equiv. KOH	Ketones (26 examples)	92%	8	12
10	Nano-Fe_2O_3 (30 mol% Fe)	135/24, 0.3 equiv. tBuOK	Ketones (12 examples)	97%	5	13
11	Ni/SiO_2-Al_2O_3 (20 mol% Ni)	175/24, 0.1 equiv. K_3PO_4	Ketones (26 examples)	93	4	14

6. In Page 9, the high-resolution Co 2p XPS spectrum is interpreted as containing only Co^{2+} species, with Co $2p_{3/2}$ peaks at 780.43 and 782.63 eV and a satellite at 790.80 eV (Fig. 4e). However, the deconvoluted spectrum clearly suggests the presence of at least two cobalt oxidation states. The fitted components are more consistent with a mixed Co^{2+}/Co^{3+} state rather than a single Co^{2+} species. This assignment should be revisited and corrected.

Reply: We thank the Reviewer for this careful observation. Upon re-evaluating the deconvolution of the Co 2p spectrum, we agree that a mixed oxidation state is more accurate. The XPS assignment and the corresponding discussion in the manuscript (Fig. 4e) have been revised to reflect a mixed Co^{2+}/Co^{3+} state.

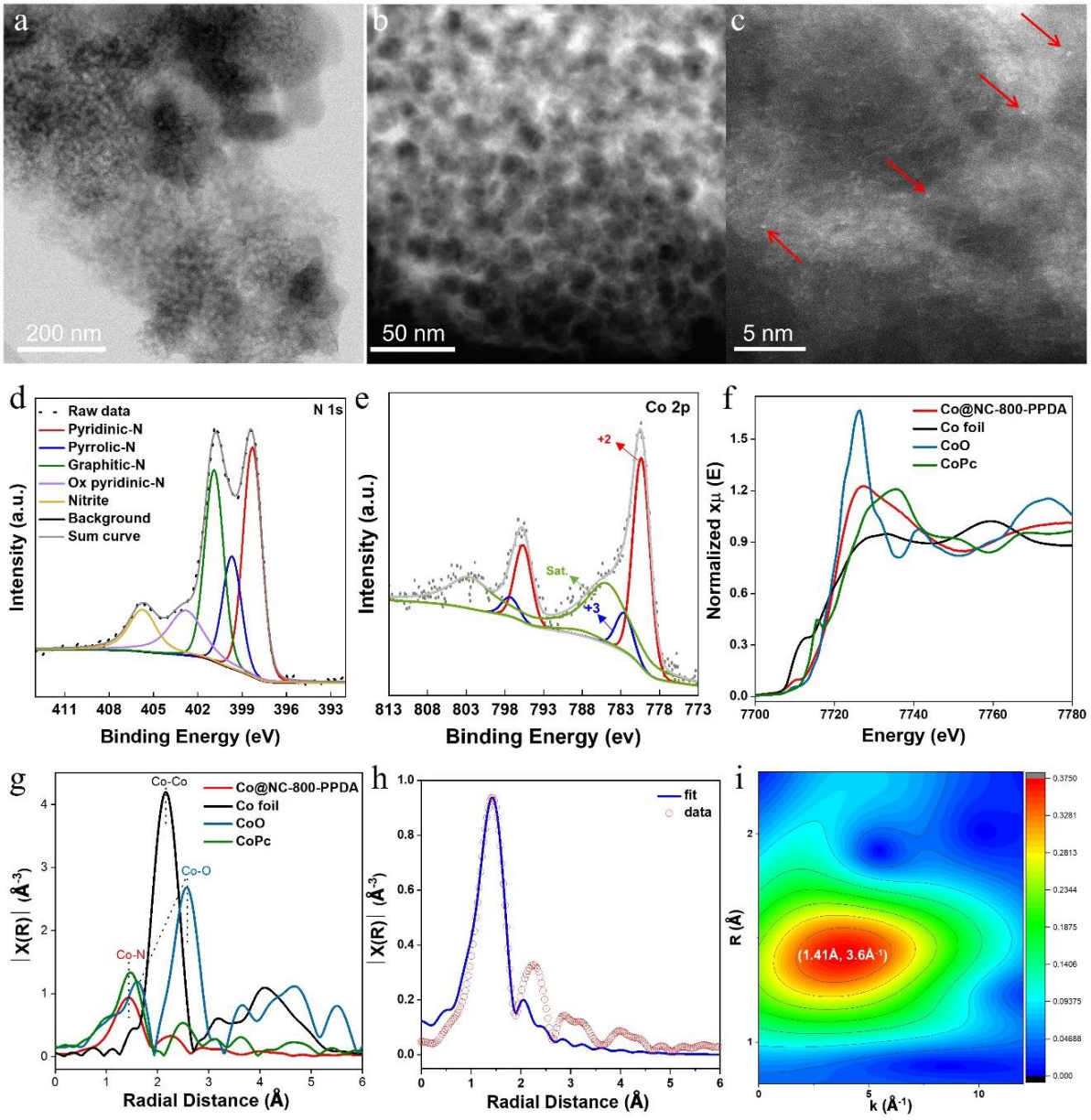


Fig. 4. Selected structural characterization of Co@NC-800-PPDA. (a, b) Overview and (c) high resolution HAADF-STEM images (Co single atoms are marked by red arrows); XP spectra for (d) N 1s, (e) Co 2p; (f) XANES and (g) FT-EXAFS and reference samples; (i) WT of Co@NC-800-PPDA.

7. Minor issues related to clarity and presentation remain and should be addressed, including ensuring

that all abbreviations are defined upon first use and correcting typographical errors (e.g., “aliphatic ahools”).

Reply: We carefully checked the paper and changed these issues accordingly.

Reply to the comments of Reviewer-3

In this manuscript, the author demonstrated that a novel and effective heterogeneous Co@NC-800-PPDA catalyst via pyrolysis of poly(p-phenylenediamine) enables excellent performance for borrowing hydrogen C-alkylation of ketones, alcohols, and lignin-derived feedstocks. The C-alkylation of lignin-derived feedstocks using alcohols as alkyl source is green and sustainable relative to halogenated compounds or organometallic reagents, so this work is of great significance. Compared to the previous reports, this synthetic protocol development of novel and effective Co@NC-800-PPDA catalyst which can be reused 6 times without obvious deactivation. A series of alcohol, and lignin-derived feedstocks were suitable for this heterogeneous cobalt SAC. Thus, **I strongly recommend to publish it in the journal of Nat. Commun. after solving the following questions**:

Reply: We thank the Reviewer for recognizing the significance of our work, especially for biomass valorization, and for recommending its publication.

1. the authors reported a Co@NC-800-PPDA catalyst via pyrolysis of poly(p-phenylenediamine), explain the reasons for the use of the poly(p-phenylenediamine) as C and N sources for the Co@NC-800-PPDA catalyst. Have you tried other catalytic systems? it will inspire the reader on how to design new catalytic material for the reaction.

Reply: We chose PPDA for its high density of nitrogen functionalities and rigid framework, which promotes isolated Co-N_4 sites. We have added a discussion comparing it to the PANI-derived system (Co@NC-800-PANI), which showed lower activity, highlighting the importance of the precursor’s molecular structure in catalyst design.

2. Supplementary Table 6, SI, KOMe (WM=70) shows a better performance than K_3PO_4 (WM=212), and 93% 3 and 95% 5 obtained. In the view of the mass ration of base to raw, KOMe is favorable. Why chose K_3PO_4 as the optimized base for the reaction?

Reply: While KOMe is highly active, it is a much stronger and more expensive base that can compromise selectivity and functional group compatibility. We have clarified in the manuscript that K_3PO_4 was

chosen as the optimal base to provide milder, more general conditions with better reproducibility and selectivity across a broad substrate scope.

3. In the reaction of Figure 3, 2.0 equiv. furfuryl alcohol was used, one equiv. furfuryl alcohol was converted the target product. What are the finally products of another other equiv. furfuryl alcohol? Do you observe the over-alkylation by-products via over-C-allylation of 2 with the product 3, or etherification by-product via reaction of obtained phenol 5 with furfuryl alcohol 2?

Reply: In our system, the excess alcohol facilitates hydrogen transfer and drives the BH process. We have clarified that the excess equivalent mainly undergoes dehydrogenation to the corresponding aldehyde. No significant over-alkylation or etherification by-products were detected under our optimized conditions. The use of excess primary alcohol is necessary to facilitate sufficient hydrogen and to drive the BH process efficiently, and this strategy is consistent with previous works (*Chem. Sci*., 2022, **13**, 111-117; *Org. Lett.* 2017, **19**, 1080-1083), where primary alcohols are typically employed in excess to ensure smooth conversion and suppress side reactions.

4. The base additive K_3PO_4 is important for the reaction, and the performance of the Co@NC-800-PPDA catalyst observed decreased (Supplementary Table 7, entry 1), can you explore the role of K_3PO_4.

Reply: We agree that the role of the base is critical. Hence, we have expanded the discussion to explain that K_3PO_4 assists in alcohol dehydrogenation (proton abstraction) and promotes the subsequent aldol condensation step by activating carbonyl intermediates. Moreover, previous reports (*Org. Lett*. 2017, **19**, 1080-1083; *ACS Catal*. 2018, **8**, 10300-10305.) have also demonstrated that the base is critical for on BH reactions, further supporting our conclusion that K_3PO_4 is essential for such transformation.