

Single-Crystal Cobalt Phosphide Nanorods as a High-Performance Catalyst for Reductive Amination of Carbonyl Compounds

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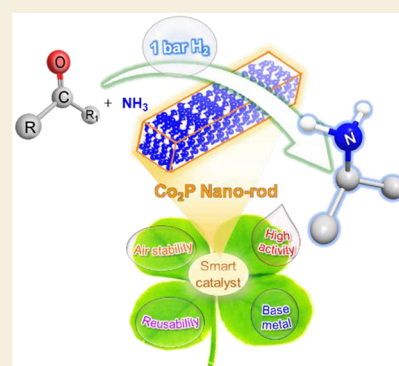
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ABSTRACT: The development of metal phosphide catalysts for organic synthesis is still in its early stages. Herein, we report the successful synthesis of single-crystal cobalt phosphide nanorods (Co₂P NRs) containing coordinatively unsaturated Co–Co active sites, which serve as a new class of air-stable, highly active, and reusable heterogeneous catalysts for the reductive amination of carbonyl compounds. The Co₂P NR catalyst showed high activity for the transformation of a broad range of carbonyl compounds to their corresponding primary amines using an aqueous ammonia solution or ammonium acetate as a green amination reagent at 1 bar of H₂ pressure; these conditions are far milder than previously reported. The air stability and high activity of the Co₂P NRs is noteworthy, as conventional Co catalysts are air-sensitive (pyrophorous) and show no activity for this transformation under mild conditions. P-alloying is therefore of considerable importance for nanoengineering air-stable and highly active non-noble-metal catalysts for organic synthesis.

KEYWORDS: cobalt, phosphide, reductive amination, aldehyde, ketone



INTRODUCTION

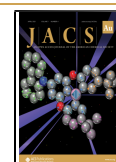
Heterogeneous metal catalysts are a part of key technologies in automobile exhaust gas cleaning, energy conversion, and storage, including fuel cells, water-splitting, N₂ reduction, and other industrially important reactions, such as petrochemical manufacturing and fine chemical synthesis.^{1–4} The precise fabrication of metal nanomaterials through control over their morphologies (size and shape), doping with heteroatoms, and alloying with additional metals or non-metal elements considerably improves their catalytic performances.^{5–8} In this context, less common metal–metalloid alloys, specifically metal phosphide nanoalloys, have attracted attention as a new class of hydrotreating catalysts and electro- and photocatalysts for energy conversion.^{6,9–14} It is also predicted that the introduction of P atoms into metals can significantly improve the catalytic properties of conventional metal catalyst systems for energy and environmental applications.¹⁵ However, the use of metal phosphide catalysts in organic synthesis is still in the early stages of development, as examples of these are limited.^{16–20} Nevertheless, we recently reported the catalytic activity of nickel and cobalt phosphide nanoalloys for the transformation of biofuranic aldehydes to diketones and the hydrogenation of nitriles to primary amines, respectively, exhibiting turnover numbers (TONs) an order of magnitude higher than those of conventional non-noble-metal catalysts.^{21,22} Based on the above studies, we concluded that “phosphorus-alloying (P-alloying)” has two important roles in non-noble-metal-catalyzed organic transformations. One is its

ability to stabilize low valent metals. X-ray absorption fine structure (XAFS) studies have shown that metal phosphide nanoalloys retain their metallic states in air.^{21–23} The other is the ligand effect. Density functional theory (DFT) calculations revealed that P-alloying can modulate the electronic state of the metal species and increase its *d*-electron density near the Fermi level. This effect imparts the metal with a high ability to hydrogenate.²² Furthermore, we envisaged that P-alloying could be advantageous for the creation of well-defined catalytically active species in the crystalline metal phosphide that favor selective reactions. This is in contrast to conventional heterogeneous catalysts, which have multiple ill-defined active sites that result in inferior catalytic performance. These results encouraged us to further investigate the catalytic potential of metal phosphides in other valuable molecular transformations.

Primary amines are essential feedstocks and key intermediates in the manufacture of pharmaceuticals, dyes, polymers, and detergents.^{24–26} Reductive amination of carbonyl compounds with ammonia and hydrogen represents one of the most sustainable methods to synthesize primary amines

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with high atom efficiency, as the carbonyls and reagents are easily available and inexpensive, and theoretically, only water is formed as a byproduct. To date, various metal catalysts have been developed for reductive amination.^{27–40} Among them, low-cost and earth-abundant metal-based catalysts such as nickel and/or cobalt sponge metal catalysts, e.g., Raney catalysts, are widely employed in industrial reductive amination reactions.^{41–43} However, these catalysts are highly air-sensitive (pyrophorous) and easily deactivated during storage, requiring anaerobic handling to avoid oxidative degradation during the activation, operation, separation, and reuse steps of the catalysts. Moreover, these catalysts require harsh reaction conditions, e.g., high H₂ pressures, and their applicability for converting carbonyl compounds is limited. Therefore, the development of air-stable earth-abundant metal catalyst alternatives to sponge metal catalysts for the reductive amination of carbonyl compounds is highly challenging and in great demand. In this regard, significant progress was made by Beller et al., who recently reported that coating non-noble-metal nanoparticles (NPs) with N-doped carbon materials is an attractive strategy to produce air-stable non-noble-metal catalysts for various hydrogenation reactions.^{44–48} Based on this concept, air-stable and reusable Ni-, Co-, and Fe-based catalysts for reductive amination reactions were developed (Figure 1a).^{34–38} To date, there is no catalyst design strategy

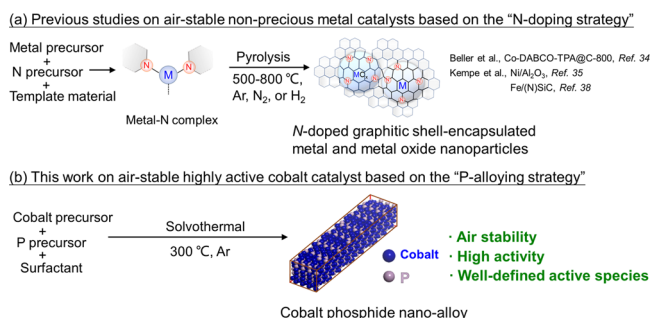


Figure 1. Air-stable non-precious metal catalysts for reductive amination based on (a) an N-doping strategy and (b) a P-alloying strategy.

available to develop air-stable base metal catalysts for reductive aminations, except for the aforementioned "N-doping strategy," and flammable ammonia gas and/or high H₂ pressures are still required to promote the amination reaction. Moreover, the active surface sites of these non-noble-metal catalysts are shielded due to encapsulation by N-doped carbon layers; thus, the stability of the NPs is achieved at the expense of their activity. Therefore, there is still considerable interest in establishing innovative, efficient, and sustainable catalyst technology to overcome the trade-off between stability and activity of non-noble-metal NPs for reductive amination. Herein, we report the novel synthesis of single-crystal cobalt phosphide nanorods (Co₂P NRs) based on the "P-alloying strategy." Co₂P NRs serve as smart catalysts, which exhibit both high activity and air stability in the reductive amination of carbonyl compounds with ammonia reagents (Figure 1b). A wide range of carbonyl compounds were converted to their corresponding primary amines with high efficiency and at a notably low H₂ pressure. This is the first example of a metal phosphide for promoting reductive amination.

RESULTS AND DISCUSSION

The Co₂P NRs were synthesized according to a previously reported method with slight modifications (e.g., the metal precursor used).²² Cobalt(II) acetylacetonate [Co(acac)₂] was added to 1-octadecene in the presence of hexadecylamine and triphenylphosphite. The mixture was stirred under an argon atmosphere, while the temperature was increased to 300 °C, which generated a black colloidal solution. The product was collected by centrifugation and washed to afford the Co₂P NRs. The representative transmission electron microscopy (TEM) images show that the prepared Co₂P NPs have a uniform nanorod morphology with a diameter of ~10 nm and length in the range of 50–150 nm (Figures 2a,b). Figure 2c

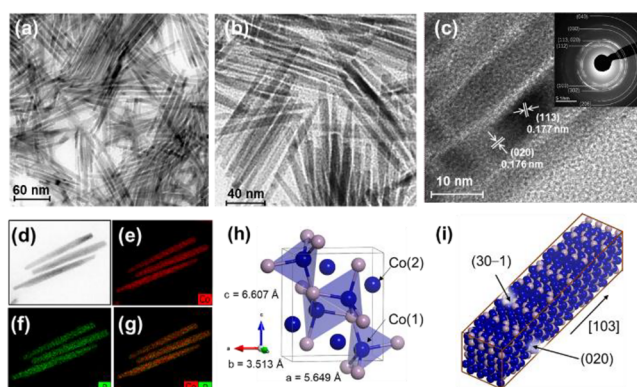


Figure 2. (a,b) TEM images of the Co₂P NRs showing a rod-like morphology. (c) HR-TEM image of the Co₂P NRs with the inset illustrating the corresponding SAED pattern. (d) STEM image of the Co₂P NRs. Elemental mapping images of (e) Co and (f) P. (g) Composite overlay image of (e) and (f). (h) Unit cell of Co₂P (ICSD 94379). (i) Proposed crystal structure of the Co₂P NR.

displays a high-resolution TEM (HR-TEM) image that includes distinct fringes. The measured lattice fringe *d*-spacing values are 0.176 and 0.177 nm, which correspond to the (020) and (113) surfaces, respectively (Figure 2c). Hence, the growth direction is assigned to [103], which is different from the growth direction of the Co₂P structure previously reported.⁴⁹ Figure 2c (inset) shows the selected area electron diffraction (SAED) patterns of the NRs (Figure S1). The diffraction pattern can be indexed based on the Co₂P orthorhombic structure (space group: *Pnma*; lattice parameters: *a* = 5.649 Å, *b* = 3.513 Å, *c* = 6.607 Å), revealing the single-crystalline nature of the synthesized Co₂P NRs (Figure 2h).⁵⁰ Elemental mapping using scanning transmission electron microscopy (STEM) confirms the homogeneous distribution of the Co and P elements (Figures 2e–g). In addition, the corresponding energy-dispersive X-ray (EDX) spectrum demonstrates that the stoichiometric Co-to-P ratio is close to 2:1 (Figure S2). These results clearly support the successful synthesis of single-crystal Co₂P NRs containing large amounts of Co(2) content on the surfaces ((020), (30-1)), as illustrated in Figure 2i.

To gain more insight into the Co species present in the Co₂P NRs, Co *K*-edge XAFS analysis was conducted in air atmosphere. The edge positions of the X-ray absorption near-edge structure (XANES) spectra of the Co₂P NRs, bulk Co₂P, and CoP NPs are presented in Figure 3. The spectra of the cobalt phosphides with varying P contents differ from that of CoO but are similar to that of Co foil, indicating that the Co

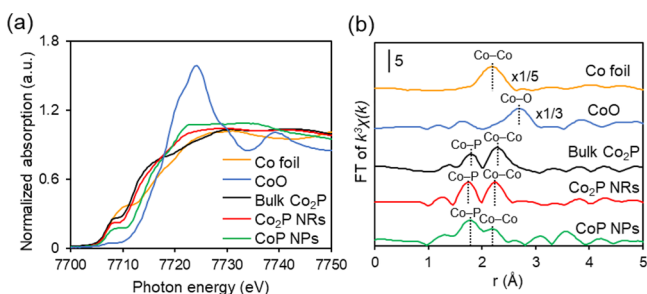


Figure 3. Co K-edge (a) XANES and (b) FT-EXAFS spectra of Co foil, CoO, bulk Co₂P, Co₂P NRs, and CoP NPs.

species in the cobalt phosphides is in the metallic state (Figure 3a). This air-stable metallic nature of the Co₂P NRs is well supported by the X-ray photoelectron spectroscopy (XPS) analysis of the air-exposed Co₂P NRs. The obtained Co 2p spectrum includes peaks at 777.8 and 792.8 eV, which are close to or slightly more negative than those of metallic Co 2p_{3/2} (777.9 eV) and Co 2p_{1/2} (793.5 eV) (Figure S3). Figure 3b shows the Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra of the Co foil, CoO, bulk Co₂P, Co₂P NRs, and CoP NPs. The Co–P and Co–Co bonds appear at 1.6–2.0 and 2.0–2.5 Å, respectively, for bulk Co₂P, the Co₂P NRs, and CoP NPs. The absence of Co–O bonds indicates that the Co₂P NRs are not oxidized in air, which is consistent with the XANES and XPS analysis results (Figures 3a and S3). Curve fitting analysis was conducted to determine the local structure of the Co₂P NRs. The Co₂P NRs and cobalt phosphide references have longer Co–Co bonds (2.56–2.60 Å) than Co foil (2.49 Å) (Table S1), because the Co–Co bonds are present in the tetrahedral CoP₄ network with vertex and edge sharing in orthorhombic Co₂P (Figure 2h). The noticeable difference between the Co₂P NRs and bulk Co₂P is the coordination number (CN) ratio, CN_{Co–Co}/CN_{Co–P}. The CN_{Co–Co}/CN_{Co–P} ratio (1.6) of the Co₂P NRs is smaller than that of bulk Co₂P (2.0), with the ideal value (1.8) calculated from the crystal structure of orthorhombic Co₂P. The small CN_{Co–Co}/CN_{Co–P} ratio of the Co₂P NRs indicates that a high number of coordinatively unsaturated Co–Co sites is present on the nanorod surfaces, which is induced by the formation of the rod-shape morphology with a high content of Co(2), as shown in Figure 2i.

Initially, the catalytic activity of the Co₂P NRs was investigated for the reductive amination of a model substrate, benzaldehyde (1a), in water using three types of amination sources (an aqueous ammonia solution (aq. NH₃), gaseous ammonia (NH₃ gas), and ammonium acetate (NH₄OAc)) at 10 bar H₂ and 100 °C for 10 h (Table 1). Notably, the Co₂P NRs showed high catalytic activities when using aq. NH₃ and NH₃ gas, producing the corresponding benzylamine (2a) as the sole product in 93 and 88% yields, respectively (entries 1 and 2), while NH₄OAc provided a low yield of 2a, accompanied by the formation of benzyl alcohol (4a) (entry 3). At a lower H₂ pressure of 5 bar, the Co₂P NRs also generated high 2a yields when using aq. NH₃ (entry 4). The Co₂P NRs were even active at just 1 bar of H₂ pressure, selectively affording 2a in a high yield (entry 5). This is the first example of a cobalt catalyst that can promote reductive amination under ambient H₂ pressure. A comparison experiment between the Co₂P NRs and state-of-the-art Ni/Al₂O₃³⁵ under the same ambient H₂ pressure conditions was also

Table 1. Reductive Amination of Benzaldehyde with Co₂P NRs and Other Cobalt Catalysts^a

entry	catalyst	H ₂	NH ₃ source	time (h)	yield (%) ^b		
					2a	3a	4a
1	Co ₂ P NRs	10	aq. NH ₃	10	93	0	0
2 ^c	Co ₂ P NRs	10	NH ₃ gas	10	88	0	0
3 ^d	Co ₂ P NRs	10	NH ₄ OAc	10	15	0	73
4	Co ₂ P NRs	5	aq. NH ₃	10	94	0	0
5	Co ₂ P NRs	1	aq. NH ₃	12	90	0	1
6 ^e	Co ₂ P NRs	40	aq. NH ₃	48	87	0	0
7	bulk Co ₂ P	1	aq. NH ₃	12	0	0	0
8	CoP NPs	1	aq. NH ₃	12	0	12	0
9	sponge Co	1	aq. NH ₃	12	0	11	3
10	Co/SiO ₂	1	aq. NH ₃	12	0	0	0
11	Co/SiO ₂ -Red	1	aq. NH ₃	12	0	0	0

^aReaction conditions: Co catalyst (Co: 0.05 mmol), benzaldehyde (0.5 mmol), aq. NH₃ 25% (3 mL), 100 °C. ^bDetermined by gas chromatography–mass spectrometry (GC–MS) using an internal standard. ^cNH₃ gas (2.5 bar), water (3 mL). ^dNH₄OAc (0.2 g), water (3 mL). ^eCo₂P NRs (Co: 0.02 mmol), benzaldehyde (1.0 mmol), aq. NH₃ 25% (3 mL), room temperature (25 °C), 48 h.

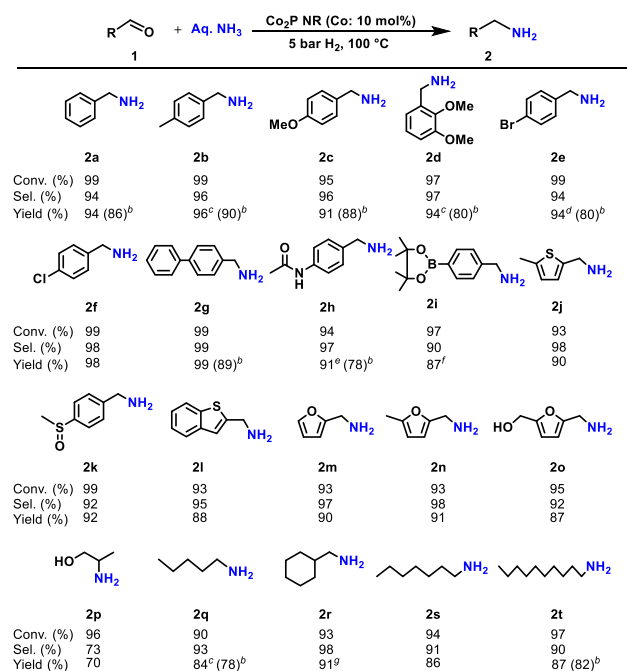
carried out, and the Co₂P NRs showed a higher yield (79 vs 6%) of 2a, revealing the superior activity of the Co₂P NRs (Scheme S1). We further investigated the catalytic potential of the Co₂P NRs at room temperature using a 2 mol % catalyst loading. The Co₂P NRs could catalyze the reductive amination of 1a at room temperature, producing 2a in 87% yield (entry 6); this is the first example of non-noble-metal-catalyzed reductive amination under ambient temperature conditions. These results clearly demonstrate the distinct performance of the Co₂P NRs from reported non-noble-metal catalysts requiring high H₂ pressures or high temperatures (Table S2 and Scheme S1).

With the Co₂P NRs in hand, the reductive amination of functionalized aldehydes was investigated using aq. NH₃ in H₂ atmosphere; the results are shown in Scheme 1. The Co₂P NRs exhibited high activity toward various aromatic and aliphatic aldehydes, producing the corresponding primary amines in high yields. Furthermore, various functional groups, such as halogen, methoxy, amide, and boronic ester moieties, were tolerant under these reaction conditions, providing the corresponding primary amines in excellent yields. Although it is well-known that sulfur compounds often strongly coordinate to the active sites of metals, resulting in significant deactivation of the catalysts, the Co₂P NR catalyst could be used for sulfur-containing carbonyl substrates such as 1j, 1k, and 1l.

Moreover, biomass-derived substrates, such as 1m, 1n, 1o, and 1p, were transformed to their corresponding primary amines in high yields.

The applicability of the Co₂P NRs was further explored in the reductive aminations of ketones, which is more challenging than that of aldehydes owing to the hydrogenation of more sterically hindered imine intermediates. Screening of the amination reagents in acetophenone amination revealed that NH₄OAc in ethanol provided the best corresponding amine yield (83%) and selectivity (100%), while using aq. NH₃ and NH₃ gas resulted in moderate amine yields (Table S3). Further screening experiments revealed that a Co₂P NR/ketone/NH₄OAc ratio of 1:10:60 in ethanol provided the optimal

Scheme 1. Substrate Scope for the Co₂P NR-Catalyzed Reductive Amination of Aldehydes with Aqueous NH₃^a



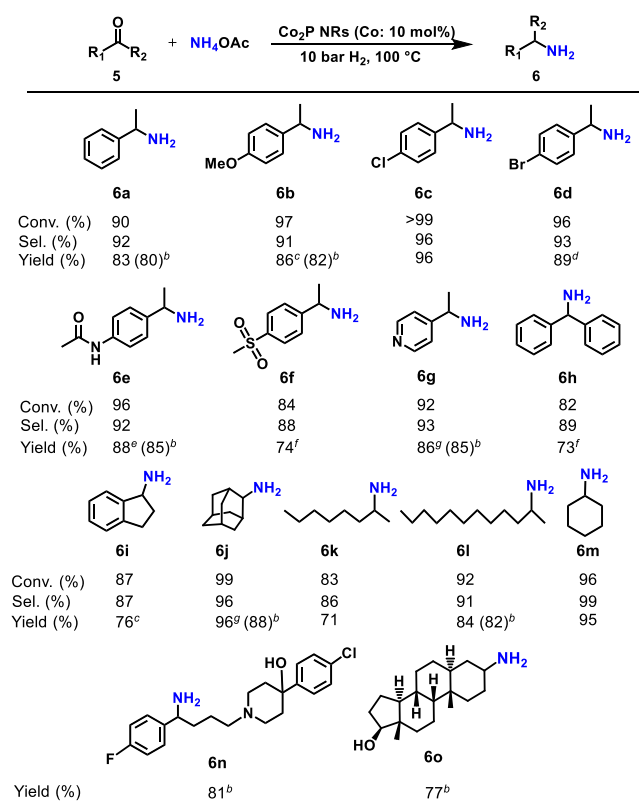
^aReaction conditions: Co₂P NRs (4.0 mg), aldehyde (0.5 mmol), aq. NH₃ 25% (3 mL), 5 bar H₂, 100 °C, 10 h. Yields were determined by GC–MS using an internal standard. ^bIsolated yield as a hydrochloride salt. ^c120 °C, 6 h. ^d70 °C. ^e80 °C, 10 bar H₂. ^f80 °C. ^gAq. NH₃ 25% (5 mL), 120 °C.

reaction conditions (Table S3). The Co₂P NRs were highly active for a wide range of ketones under the optimized conditions (Scheme 2). Aromatic and heteroaromatic ketones bearing diverse functional groups, such as methoxy, halogen, amide, methyl, and sulfone functionalities, were efficiently aminated. Aliphatic and alicyclic ketones were also converted to their corresponding primary branched amines in high yields. Moreover, the Co₂P NRs could aminate structurally complex ketones including steroid-based molecules, such as **5n** and **5o**, demonstrating the prominent catalytic activity of the Co₂P NRs.

To investigate additional advantages of the use of the Co₂P NRs, some typical experiments were performed. Scheme 3 shows the substrate generality of the present amination method using the Co₂P NRs at 1 bar H₂ pressure. Several aldehydes and ketones were converted to their corresponding primary amines in high yields, demonstrating that the use of the Co₂P NRs provides a convenient and general amination method for carbonyl compounds under mild reaction conditions.

The Co₂P NRs operated well under scale-up conditions: 2.4 g of **1a** was aminated to produce the corresponding hydrochloride salt in 83% yield with a high turnover number (TON) that exceeds 1000 at 40 bar H₂ and 130 °C (Scheme 4). This TON value is the highest among homogeneous and heterogeneous non-noble-metal-based catalysts developed to date, demonstrating the distinct activity and stability of the Co₂P NRs, even with prolonged heating and elevated temperatures (Table S2). Another advantage of the Co₂P NRs is their convenient recyclability and high reusability. Conventional non-noble-metal-based catalysts are generally

Scheme 2. Substrate Scope for the Co₂P NR-Catalyzed Reductive Amination of Ketones with Ammonium Acetate^a

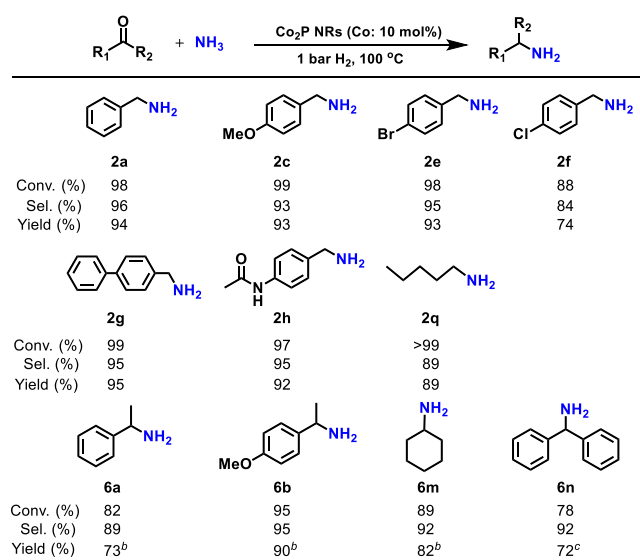


^aReaction conditions: Co₂P NRs (4.0 mg), ketone (0.5 mmol), NH₄OAc (0.2 g), ethanol (3 mL), 10 bar H₂, 100 °C, 12 h. Yields were determined by GC–MS using an internal standard. ^bIsolated yield as a hydrochloride salt. ^cNH₄OAc (0.1 g), 20 bar H₂, 110 °C. ^d110 °C. ^eNH₄OAc (0.1 g), 80 °C. ^f20 bar H₂, 110 °C. ^gNH₄OAc (0.1 g).

sensitive to air and require strict anaerobic conditions during the recycling process. In contrast, after the reaction, the Co₂P NRs were easily recovered by simple filtration under air and reused without loss of activity, even after the fourth cycle, showing high durability (Figure 4). We further investigated the initial reaction rate during the recycling experiments. Similar reaction rates (gray diamonds in Figure 4) were achieved when using the reused catalyst and the fresh catalyst. Furthermore, TEM images of the used Co₂P NRs reveal that the Co₂P NRs does not aggregate and the size and shape of the Co₂P NRs are unchanged (Figure S4). No significant changes are observed in the Co₂P NR catalyst after reuse, as confirmed by EDX, X-ray diffraction, XANES, EXAFS, and curve fitting (Figures S2, S5, S6, S7, and S8, respectively). These analyses strongly prove the high stability of the Co₂P NRs.

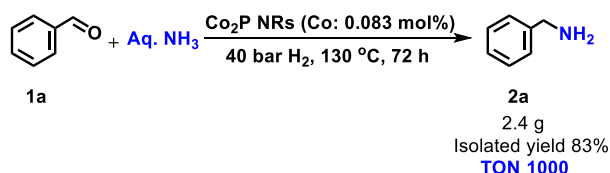
Finally, the reaction pathway of the Co₂P NR-catalyzed reductive amination was investigated by monitoring the products. The time-course data of the benzaldehyde amination (**1a**) with aq. NH₃ and H₂ using the Co₂P NRs show that the amount of **1a** significantly decreases at the initial stage with the production of the *N*-benzylidenebenzylamine intermediate (**3a**) through the condensation of **1a** and benzylamine (**2a**) (Figure 5). The maximum yield of **3a** is obtained after 2 h, which then gradually decreases with an increase in the yield of **2a**, indicating that the transformation of **3a** to **2a** is the rate-determining step. Based on these results, a possible reaction

Scheme 3. Reductive Amination of Carbonyl Compounds by the Co₂P NRs at 1 bar H₂^a



^aReaction conditions: Co₂P NRs (4.0 mg), substrate (0.5 mmol), 1 bar H₂, aq. NH₃ 25% (3 mL), 100 °C, 12 h. Yields were determined by GC–MS using an internal standard. ^bNH₄OAc (0.1 g), ethanol (3 mL). ^cNH₄OAc (0.15 g), ethanol (3 mL), 110 °C, 20 h.

Scheme 4. Gram-Scale Experiment of the Reductive Amination of 1a Using the Co₂P NRs^a



^aReaction conditions: Co₂P NRs (1.1 mg, Co: 0.018 mmol), 1a (2.4 g), aq. NH₃ 25% (40 mL), ethanol (20 mL), 40 bar H₂, 130 °C, 72 h.

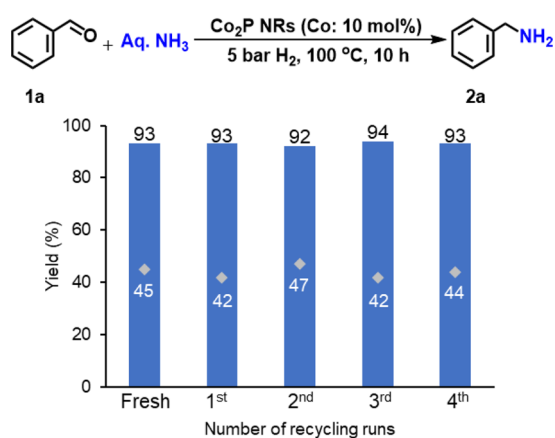


Figure 4. Reusability of the Co₂P NR-catalyzed reductive amination of 1a with aq. NH₃. Reaction conditions: Co₂P NRs (4.0 mg), 1a (0.5 mmol), aq. NH₃ 25% (3 mL), 5 bar H₂, 100 °C, 10 h. The initial reaction rate experiments (gray diamonds) were conducted under the same reaction conditions for 5 h. Yields were determined by GC–MS using an internal standard.

pathway for the transformation of 1a to 2a using the Co₂P NRs is proposed, as shown in Scheme 5. First, the condensation of

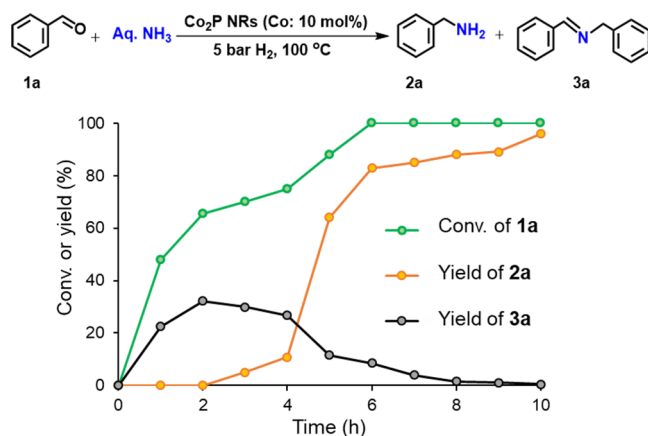
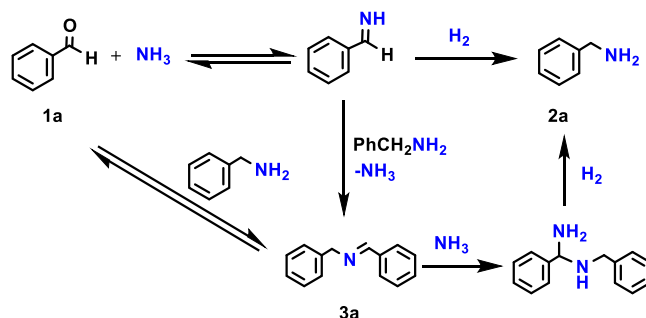


Figure 5. Time-course data of the Co₂P NR-catalyzed reductive amination of 1a with aq. NH₃. Reaction conditions: Co₂P NRs (4.0 mg), 1a (0.5 mmol), aq. NH₃ 25% (3 mL), 5 bar H₂, 100 °C, 10 h. Yields were determined by GC–MS using an internal standard.

Scheme 5. Possible Reaction Pathway for the Co₂P NR-Catalyzed Transformation of Benzaldehyde (1a) to Benzylamine (2a)



1a and NH₃ produces phenylmethanimine, which is then hydrogenated to 2a. Then, the condensation of 1a and 2a rapidly generates 3a. Subsequently, 3a is gradually transformed into 2a. It is reported that the addition of NH₃ to 3a forms an unstable geminal amine, which is then hydrogenated to 2a.⁵¹ This is well-supported by the control experiments using 3a as starting material, where the yield of 2a increases in the presence of NH₃ (Figure S9). The high catalytic activity of the Co₂P NRs is related to its high hydrogenation ability, i.e., the hydrogenation of phenylmethanimine to 2a and 3a to 2a, which is derived from the rod-shaped morphology providing a high number of coordinatively unsaturated Co–Co surface sites. Furthermore, our recent study using DFT calculations revealed that P-alloying and nanosizing of Co significantly increases the *d*-electron density of Co near the Fermi level, which provides the high hydrogenation ability of the Co₂P nanoparticles.²² Hence, the Co₂P NRs accelerate the hydrogenation of the intermediate imines and 3a, resulting in high catalytic activity for the reductive amination of carbonyl compounds.

CONCLUSION

We synthesized novel single-crystal Co₂P NRs, which retain their air-stable metallic nature, containing coordinatively unsaturated Co–Co active sites. The well-ordered Co₂P NRs serve as highly active and reusable heterogeneous catalysts for the reductive amination of various carbonyl compounds to the

corresponding primary amines using NH_3 sources and H_2 . The observed catalytic activity is superior to that of previously reported catalyst systems. Typically, the Co_2P NRs promote the amination under relatively mild conditions, even at 1 bar H_2 pressure. This is the first example of both a metal phosphide promoting reductive amination and a cobalt catalyst operating at ambient H_2 pressure. Furthermore, this solid catalyst is recoverable and reusable while maintaining its high catalytic activity and selectivity. Our findings demonstrate that the “P-alloying strategy” is a promising nanotechnology to develop a new class of stable and highly active non-noble-metal catalysts that can substitute conventional sponge metal catalysts. We believe that these less common metal phosphides also exhibit unique and high-performance activity in a broader field of reactions. “P-alloying” therefore provides a new avenue for greener and more sustainable synthesis of valuable chemicals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.1c00125>.

Experimental details and catalyst characterization results (PDF)

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<https://pubs.acs.org/10.1021/jacsau.1c00125>

Author Contributions

T. Mit. wrote the paper and coordinated all the experimental investigations. M.S. designed and performed the experiments. S.F. and J.Y. performed the TEM measurements and analysis. S. Yamaz. performed the XAFS analysis. S. Yamag., K.N., and T. Miz. discussed the experiments and results. All authors commented critically on the manuscript and approved the final manuscript.

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Notes

The authors declare no competing financial interest.

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