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Article

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

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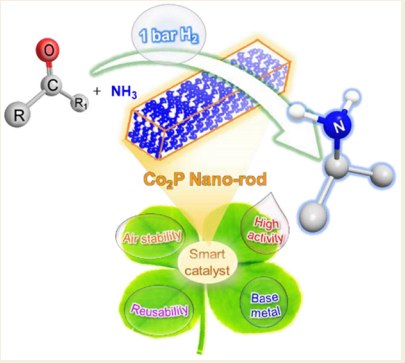
ABSTRACT: The development of metal phosphide catalysts for organic synthesis is still in its early stages. Herein, we report the successful synthesis of single-crystal cobalt phosphide nanorods (Co_2P NRs) containing coordinatively unsaturated Co−Co active sites, which serve as a new class of air-stable, highly active, and reusable heterogeneous catalysts for the reductive amination of carbonyl compounds. The Co_2P 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 H_2 pressure; these conditions are far milder than previously reported. The air stability and high activity of the Co_2P 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, N_2 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 H_2 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

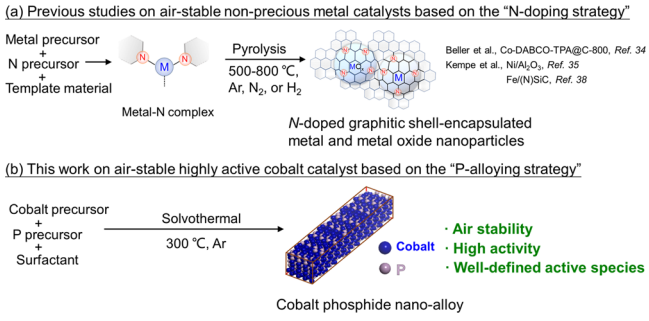

Figure 1. Air-stable non-precious metal catalysts for reductive amination based on (a) an N-doping strategy and (b) a P-alloying strategy.

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 H_2 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 (Co_2P NRs) based on the "P-alloying strategy." Co_2P 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 H_2 pressure. This is the first example of a metal phosphide for promoting reductive amination.

RESULTS AND DISCUSSION

The Co_2P 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 Co_2P NRs. The representative transmission electron microscopy (TEM) images show that the prepared Co_2P 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

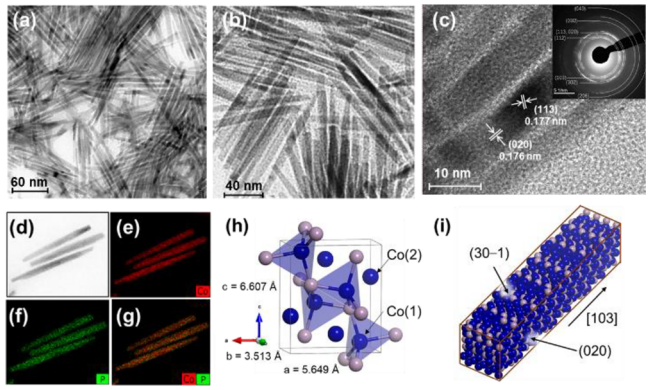

Figure 2. (a,b) TEM images of the Co_2P NRs showing a rod-like morphology. (c) HR-TEM image of the Co_2P NRs with the inset illustrating the corresponding SAED pattern. (d) STEM image of the Co_2P NRs. Elemental mapping images of (e) Co and (f) P. (g) Composite overlay image of (e) and (f). (h) Unit cell of Co_2P (ICSD 94379). (i) Proposed crystal structure of the Co_2P 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 Co_2P 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 Co_2P 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 Co_2P 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 Co_2P 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 Co_2P 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 Co_2P NRs, bulk Co_2P, 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

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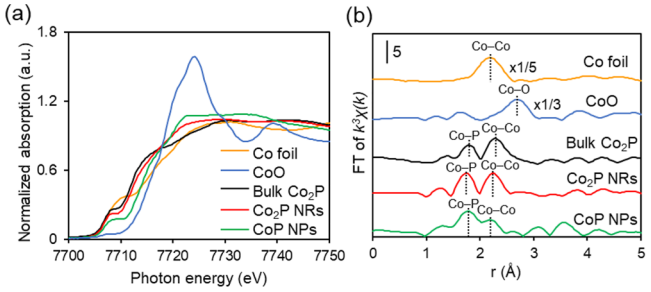
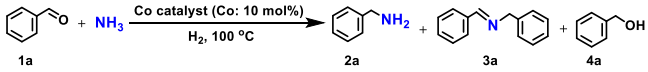


Figure 3. Co *K*-edge (a) XANES and (b) FT-EXAFS spectra of Co foil, CoO, bulk Co_2P, Co_2P NRs, and CoP NPs.

species in the cobalt phosphides is in the metallic state (Figure 3a). This air-stable metallic nature of the Co_2P NRs is well supported by the X-ray photoelectron spectroscopy (XPS) analysis of the air-exposed Co_2P 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 Co_2P, Co_2P 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 Co_2P, the Co_2P NRs, and CoP NPs. The absence of Co−O bonds indicates that the Co_2P 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 Co_2P NRs. The Co_2P 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 CoP_4 network with vertex and edge sharing in orthorhombic Co_2P (Figure 2h). The noticeable difference between the Co_2P NRs and bulk Co_2P is the coordination number (*CN*) ratio, CN_{Co-Co}/CN_{Co-P}. The CN_{Co-Co}/CN_{Co-P} ratio (1.6) of the Co_2P NRs is smaller than that of bulk Co_2P (2.0), with the ideal value (1.8) calculated from the crystal structure of orthorhombic Co_2P. The small CN_{Co-Co}/CN_{Co-P} ratio of the Co_2P 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 Co_2P 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. NH_3), gaseous ammonia (NH_3 gas), and ammonium acetate (NH_4OAc)) at 10 bar H_2 and 100 °C for 10 h (Table 1). Notably, the Co_2P NRs showed high catalytic activities when using aq. NH_3 and NH_3 gas, producing the corresponding benzylamine (**2a**) as the sole product in 93 and 88% yields, respectively (entries 1 and 2), while NH_4OAc provided a low yield of **2a**, accompanied by the formation of benzyl alcohol (**4a**) (entry 3). At a lower H_2 pressure of 5 bar, the Co_2P NRs also generated high **2a** yields when using aq. NH_3 (entry 4). The Co_2P NRs were even active at just 1 bar of H_2 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 H_2 pressure. A comparison experiment between the Co_2P NRs and state-of-the-art Ni/Al_2O_3[35] under the same ambient H_2 pressure conditions was also

Table 1. Reductive Amination of Benzaldehyde with Co_2P NRs and Other Cobalt Catalysts[a]



					yield (%)[b]		
entry	catalyst	H_2	NH_3 source	time (h)	**2a**	**3a**	**4a**
1	Co_2P NRs	10	aq. NH_3	10	93	0	0
2[c]	Co_2P NRs	10	NH_3 gas	10	88	0	0
3[d]	Co_2P NRs	10	NH_4OAc	10	15	0	73
4	Co_2P NRs	5	aq. NH_3	10	94	0	0
5	Co_2P NRs	1	aq. NH_3	12	90	0	1
6[e]	Co_2P NRs	40	aq. NH_3	48	87	0	0
7	bulk Co_2P	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

[a]Reaction conditions: Co catalyst (Co: 0.05 mmol), benzaldehyde (0.5 mmol), aq. NH_3 25% (3 mL), 100 °C. [b]Determined by gas chromatography−mass spectrometry (GC−MS) using an internal standard. [c]NH_3 gas (2.5 bar), water (3 mL). [d]NH_4OAc (0.2 g), water (3 mL). [e]Co_2P NRs (Co: 0.02 mmol), benzaldehyde (1.0 mmol), aq. NH_3 25% (3 mL), room temperature (25 °C), 48 h.

carried out, and the Co_2P NRs showed a higher yield (79 vs 6%) of **2a**, revealing the superior activity of the Co_2P NRs (Scheme S1). We further investigated the catalytic potential of the Co_2P NRs at room temperature using a 2 mol % catalyst loading. The Co_2P 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 Co_2P NRs from reported non-noble-metal catalysts requiring high H_2 pressures or high temperatures (Table S2 and Scheme S1).

With the Co_2P NRs in hand, the reductive amination of functionalized aldehydes was investigated using aq. NH_3 in H_2 atmosphere; the results are shown in Scheme 1. The Co_2P 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 Co_2P 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 Co_2P 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 NH_4OAc in ethanol provided the best corresponding amine yield (83%) and selectivity (100%), while using aq. NH_3 and NH_3 gas resulted in moderate amine yields (Table S3). Further screening experiments revealed that a Co_2P NR/ketone/NH_4OAc ratio of 1:10:60 in ethanol provided the optimal

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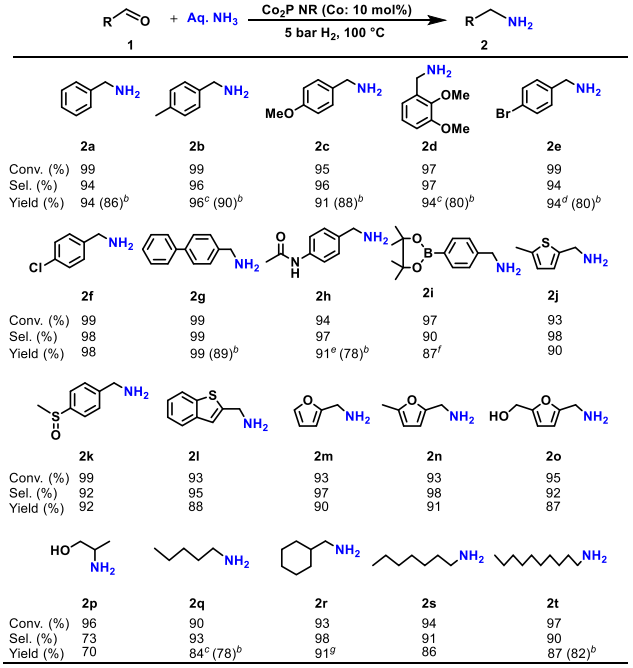
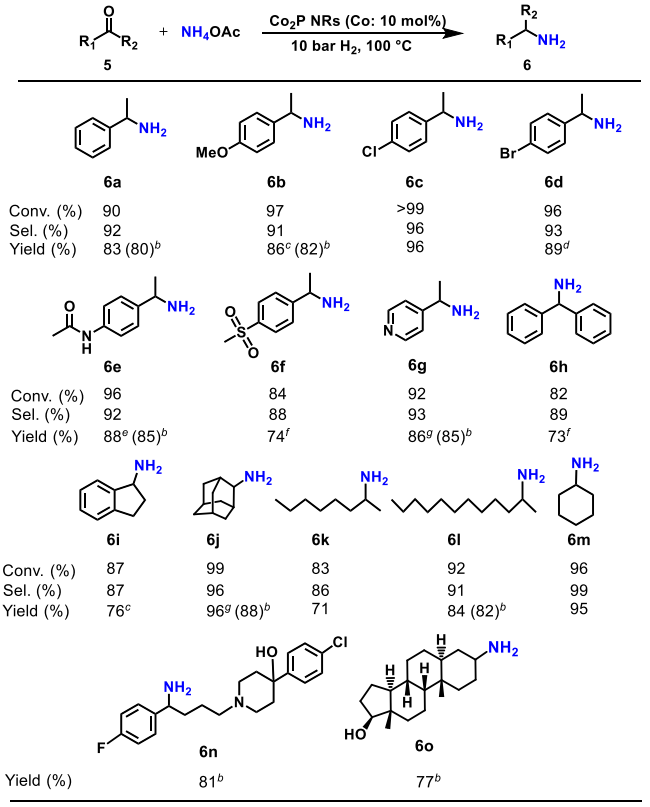
Scheme 1. Substrate Scope for the Co_2P NR-Catalyzed Reductive Amination of Aldehydes with Aqueous NH_3[a]



[a]Reaction conditions: Co_2P NRs (4.0 mg), aldehyde (0.5 mmol), aq. NH_3 25% (3 mL), 5 bar H_2, 100 °C, 10 h. Yields were determined by GC−MS using an internal standard. [b]Isolated yield as a hydrochloride salt. [c]120 °C, 6 h. [d]70 °C. [e]80 °C, 10 bar H_2. [f]80 °C. [g]Aq. NH_3 25% (5 mL), 120 °C.

Scheme 2. Substrate Scope for the Co_2P NR-Catalyzed Reductive Amination of Ketones with Ammonium Acetate[a]



[a]Reaction conditions: Co_2P NRs (4.0 mg), ketone (0.5 mmol), NH_4OAc (0.2 g), ethanol (3 mL), 10 bar H_2, 100 °C, 12 h. Yields were determined by GC−MS using an internal standard. [b]Isolated yield as a hydrochloride salt. [c]NH_4OAc (0.1 g), 20 bar H_2, 110 °C. [d]110 °C. [e]NH_4OAc (0.1 g), 80 °C. [f]20 bar H_2, 110 °C. [g]NH_4OAc (0.1 g).

reaction conditions (Table S3). The Co_2P 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 Co_2P NRs could aminate structurally complex ketones including steroid-based molecules, such as **5n** and **5o**, demonstrating the prominent catalytic activity of the Co_2P NRs.

To investigate additional advantages of the use of the Co_2P NRs, some typical experiments were performed. Scheme 3 shows the substrate generality of the present amination method using the Co_2P NRs at 1 bar H_2 pressure. Several aldehydes and ketones were converted to their corresponding primary amines in high yields, demonstrating that the use of the Co_2P NRs provides a convenient and general amination method for carbonyl compounds under mild reaction conditions.

The Co_2P 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 H_2 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 Co_2P NRs, even with prolonged heating and elevated temperatures (Table S2). Another advantage of the Co_2P NRs is their convenient recyclability and high reusability. Conventional non-noble-metal-based catalysts are generally sensitive to air and require strict anaerobic conditions during the recycling process. In contrast, after the reaction, the Co_2P 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 Co_2P NRs reveal that the Co_2P NRs does not aggregate and the size and shape of the Co_2P NRs are unchanged (Figure S4). No significant changes are observed in the Co_2P 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 Co_2P NRs.

Finally, the reaction pathway of the Co_2P NR-catalyzed reductive amination was investigated by monitoring the products. The time-course data of the benzaldehyde amination (**1a**) with aq. NH_3 and H_2 using the Co_2P 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

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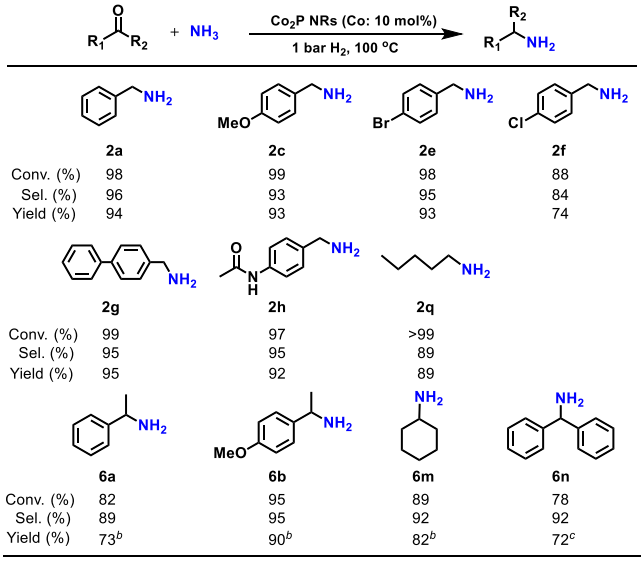
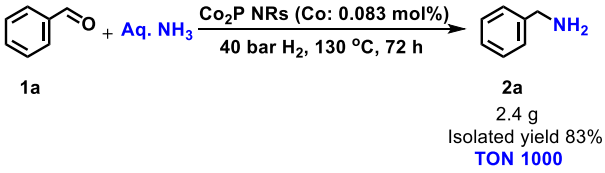
Scheme 3. Reductive Amination of Carbonyl Compounds by the Co_2P NRs at 1 bar H_2[a]



[a]Reaction conditions: Co_2P NRs (4.0 mg), substrate (0.5 mmol), 1 bar H_2, aq. NH_3 25% (3 mL), 100 °C, 12 h. Yields were determined by GC−MS using an internal standard. [b]NH_4OAc (0.1 g), ethanol (3 mL). [c]NH_4OAc (0.15 g), ethanol (3 mL), 110 °C, 20 h. [c]NH_4OAc (0.15 g), ethanol (3 mL), 110 °C, 20 h.

Scheme 4. Gram-Scale Experiment of the Reductive Amination of 1a Using the Co_2P NRs[a]



[a]Reaction conditions: Co_2P NRs (1.1 mg, Co: 0.018 mmol), **1a** (2.4 g), aq. NH_3 25% (40 mL), ethanol (20 mL), 40 bar H_2, 130 °C, 72 h.

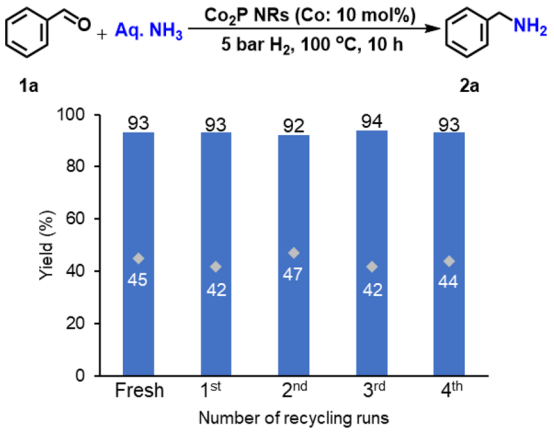


Figure 4. Reusability of the Co_2P NR-catalyzed reductive amination of **1a** with aq. NH_3. Reaction conditions: Co_2P NRs (4.0 mg), **1a** (0.5 mmol), aq. NH_3 25% (3 mL), 5 bar H_2, 100 °C, 10 h. The initial reaction rate experiments (gray diamonds) were conducted under the same reaction conditions for 5 h. Yields were determined by GC−MS using an internal standard.

pathway for the transformation of **1a** to **2a** using the Co_2P NRs is proposed, as shown in Scheme 5. First, the condensation of

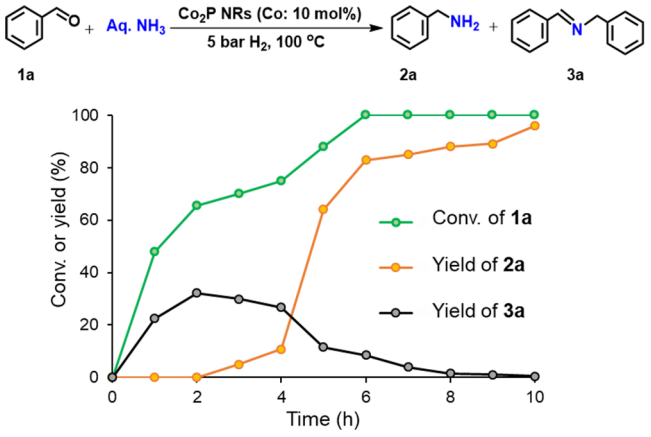
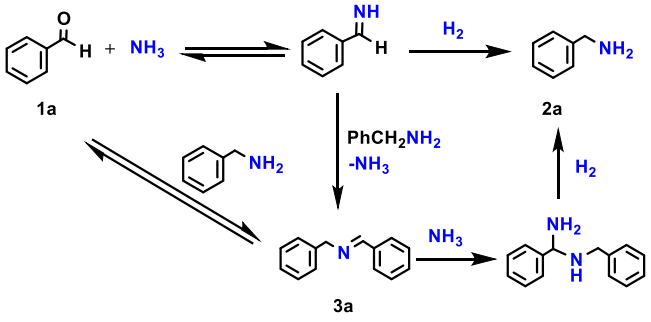


Figure 5. Time-course data of the Co_2P NR-catalyzed reductive amination of **1a** with aq. NH_3. Reaction conditions: Co_2P NRs (4.0 mg), **1a** (0.5 mmol), aq. NH_3 25% (3 mL), 5 bar H_2, 100 °C, 10 h. Yields were determined by GC−MS using an internal standard.

Scheme 5. Possible Reaction Pathway for the Co_2P NR-Catalyzed Transformation of Benzaldehyde (1a) to Benzylamine (2a)



1a and NH_3 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 NH_3 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 NH_3 (Figure S9). The high catalytic activity of the Co_2P 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 Co_2P nanoparticles.[22] Hence, the Co_2P 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 Co_2P NRs, which retain their air-stable metallic nature, containing coordinatively unsaturated Co−Co active sites. The well-ordered Co_2P NRs serve as highly active and reusable heterogeneous catalysts for the reductive amination of various carbonyl compounds to the

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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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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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