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CN-Doped Cobalt Oxide Composite: An Economic and Reusable Catalyst with Multitasking Catalytic Capability for Alkyne and Nitrile Hydrations and Nitro Reductions

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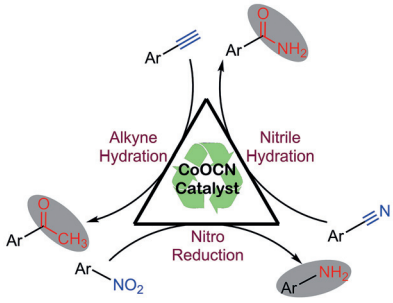

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Abstract A heterogeneous CoOCN composite was synthesized via a one-pot reaction of $[Co(NO_3)_2]$ and urea at 500 °C in a muffle furnace. The composite was fully characterized by FTIR, Raman, powder XRD, and XPS techniques. The catalyst was found to be efficient for the hydrations of aryl alkynes and nitriles under aerobic conditions. In addition, the catalyst exhibits high catalytic performance for the reduction of nitroarenes under inert gas-free conditions. This multitasking CoOCN composite was found to be highly suitable for all derivatives of nitrobenzene, alkynes, and nitriles because good to excellent yields were obtained. The catalyst was recovered quantitatively from the reaction mixture by simple filtration and consequently reused for seven consecutive cycles in all reactions without significant loss of catalytic activity. Hence, the synthesized CN-doped CoOCN composite worked as a multitasking catalyst for various value-added organic transformations, and it is highly economical and reusable for up to seven catalytic cycles without any activation, with even the last cycle producing reasonable yields of up to 48–50%.

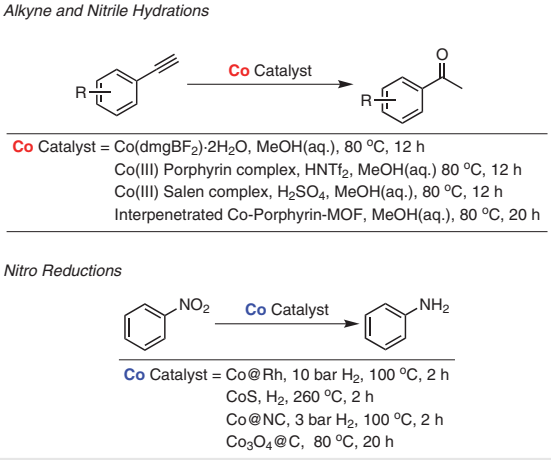
Key words heterogeneous catalysts, cobalt oxide, alkyne hydration, nitrile hydration, nitro reduction, catalysis

Catalysts offer a vast array of sustainable and effective synthetic methodologies that can be implemented on a bulk scale.[1] Catalysis is an indispensable technique for the material, active pharmaceutical ingredient (API), pharmaceutical, and chemical industries.[2] As a subset, heterogeneous catalysts had proved their significance. Easy separation, reusability, stability toward air and moisture, and facile synthesis make them highly tempting for applications within industries.[3] As the literature shows, the production of 60% of commercially relevant products and 90% of industrial processes use heterogeneous catalysts.[4] In recent decades, heterogeneous catalysts have also shown their innumerable applications in nanotechnology, biotechnology, green chemistry, and fuel cell technologies.[5] Since the 1950s, metal oxides had revolutionized the synthesis of various compounds and intermediates.[6] The catalytic synthesis of petrochemicals, steam reforming, methanol steam reforming, water gas shift, MTG process, MTO process, and hydrodesulfurization of oil distillates are some of the major industrial processes covered by 3d transition metal oxides.[7] Co_3O_4 is one of the non-endangered, low toxicity, economical metal oxides that have exceptional potential in catalysis. Moreover, the cobalt oxides are easy to synthesize, incredibly stable, heterogeneous, and reusable as catalysts for various synthetic procedures. Cobalt oxides are well known for their commercial application as catalysts in the desulfurization of oil distillates and syngas production. Despite having wide applications, the transition metal oxides are still not utilized for alkyne hydration reactions. The hydration of alkynes in aqueous media could be the easiest method for the production of methyl ketones. However, the chemical union of non-polar unsaturated hydrocarbons with polar water molecules is difficult because of their affinities.[8] A catalyst performing hydration would have to induce polarity in the hydrocarbon and facilitate the attack of the H_2O molecule.[8] Addition of water to terminal alkynes may lead to the Markovnikov or anti-Markovnikov type of addition of water.[9] These might be the possible reasons that alkyne hydration is not yet accepted as a commercial synthesis of aromatic methyl ketones.

The addition of water over alkynes to form ketones has essential applications in API industries for the synthesis of fexofenadine, benperidol, droperidol, azaperone, and other related drugs.[9] Initially, Hg-based catalysts were used, but Hg has inherent environmental side effects. Various transi-

tion metal complexes containing Ru, Pd, Rh, Pt, Ag, Au, mineral acids, and organic acids (PTSA, TFA, TFMSA) were used as homogeneous catalysts for alkyne hydration, but they were not efficient and not viable for bulk synthesis.[10–12] In the recent past, catalyst-free alkyne hydration has also been reported, but it worked at high temperatures and high-pressure conditions.[13,14]

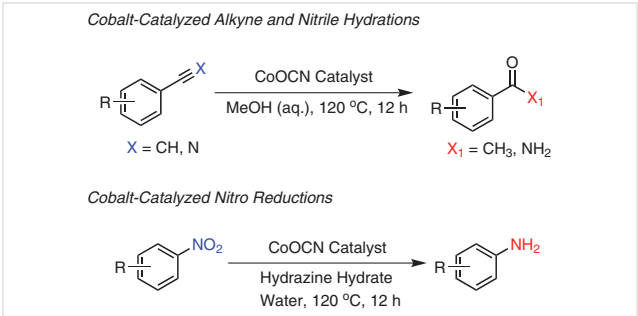
In the present decade, several cobalt complexes have been used for alkyne hydration. Few reports are available showing their efficient activity for hydration reactions. Some of the previous reports on cobalt-catalyzed alkyne hydration are depicted in Scheme 1.[15–18]



Scheme 1 Previous work on cobalt-catalyzed alkyne hydration and nitro reduction

After alkyne hydration, we next considered the reduction of nitrobenzene. The reduction process is very difficult because the nitro group reduction occurs in phases and then comes to a halt owing to the synthesis of hydroxylamine and azoarene as side products at a critical point. Catalytic transfer hydrogenation has traditionally been carried out in the presence of Ru,[19] Rh,[20] Pd,[21] or Ni[22] metal catalysts. Only a few researchers have used low-cost Co,[23] Fe,[24] or Zn.[25] Several other reducing agents, in addition to gaseous hydrogen, have been utilized to efficiently reduce nitrobenzene when employed in combination with metals, including boranes,[26] $NaBH_4$,[27] silanes,[28] and hydrazine.[29,30] Some of the heterogeneous cobalt catalyst reports for nitro reduction are shown in Scheme 1.[31–33]

All of these reports use hazardous H_2 gas as a source of hydrogen. Our procedure circumvents all of the drawbacks by employing a hydrogen-free atmosphere and provides a greener environment by using water as a solvent, rather than toxic solvents. In this paper, we wish to report the one-pot synthesis of a CoOCN composite from readily available and economical precursors. The CoOCN composite is successfully employed for the hydration of alkynes and nitriles, as well as the reduction of nitroarenes. The catalyst works heterogeneously and can be effectively reused for several catalytic cycles. Both hydration reactions work in aqueous methanol, while the reduction of nitroarenes occurred in aqueous media (Scheme 2).



Scheme 2 General scheme for the CoOCN-composite-catalyzed alkyne and nitrile hydrations and nitroarene reduction

Synthesis and Characterization of CoOCN Composite. The catalyst was synthesized by using a mixture of $Co(NO_3)_2$ (1 g) and urea (10 g), which was burned in a muffle furnace at 500 °C for 2 h in a silica crucible. The formation of the metal oxide composite was confirmed through FTIR and Raman spectroscopy (Figure 1), followed by powder XRD and XPS analysis. Moreover, FESEM images were also recorded for the bulk and surface properties (see the Supporting Information, Figure 1a–d). The FTIR characteristic peaks of the cobalt oxide composite were obtained at 571 cm^{-1} and 663 cm^{-1}, showing the presence of Co_3O_4.[34–36] Moreover, a weak band at 802 cm^{-1} corresponds to the breathing mode of CN heterocycles, and several strong bands in the range of 1200–1600 cm^{-1} centered at 1378 cm^{-1} show various stretching vibrations of triazine units.[35,37,38] The peaks at 2034 cm^{-1} and 2179 cm^{-1}correspond to the various CN bond stretching types, and the peak 3430 cm^{-1} is related to OH and adsorbed moisture.[39,40]

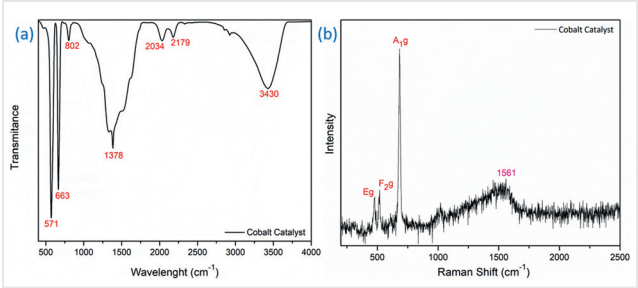


Figure 1 (a) FTIR spectrum; (b) Raman spectrum

The Raman spectrum shows weak intensity Eg and F2g bands at 472 cm^{-1} and 519 cm^{-1}, and a strong intensity A1g band is visible at 685 cm^{-1}, confirming the presence of cobalt oxide.[41] A broad asymmetric peak maxima at 1561 cm^{-1} confirms the presence of graphitic carbon.[42,43] The CoOCN composite mimics the XRD pattern of JCPDS no. 43-1003 (see the Supporting Information, Figure 2a). The elemental

composition of the CoOCN composite was confirmed through XPS analysis. The survey spectrum shows 17.64%, 44.08%, 35.34%, and 2.94% composition of cobalt, oxygen, carbon, and nitrogen, respectively (see the Supporting Information, Figure 2b). The high-resolution XPS spectra of all elements present in the catalyst show detailed information about their bonding properties. The XPS spectrum of cobalt confirms the presence of Co^{3+} and Co^{2+} in different forms (Figure 2a). Two major peaks at 779.2 eV and 794.2 eV corresponding to Co^{3+} ($2p_{1/2}$) and Co^{3+} ($2p_{3/2}$) appear owing to the presence of Co_3O_4.[41] Peaks at 780.3 eV and 795.6 eV exhibit the presence of Co^{2+} ($2p_{3/2}$) and Co^{2+} ($2p_{1/2}$) as components in the Co_3O_4, while another peak at 788.9 eV appeared as a satellite peak of Co^{2+} ($2p_{3/2}$).[40,41] The high-resolution C(1s) region composed of five distinct peaks at 284.2 eV and 284.6 eV exhibits the sp^3 and sp^2 carbon atoms, while peaks at 286.1 eV and 287.4 eV confirmed the presence of C–O and C=O (Figure 2b).[41] The XPS data show a pronounced peak of the C–N bond at 288.3 eV in the C(1s) region and also the corresponding peak in the N (1s) region at 399.8 eV.[42] Another peak in the N(1s) region at 398.3 eV is ascribed for pyridinic N, and two peaks at 402.8 eV and 406.2 eV are associated with N–O bonds (for the O(1s) and N(1s) spectra, see the Supporting Information, Figure 3).[41,42]

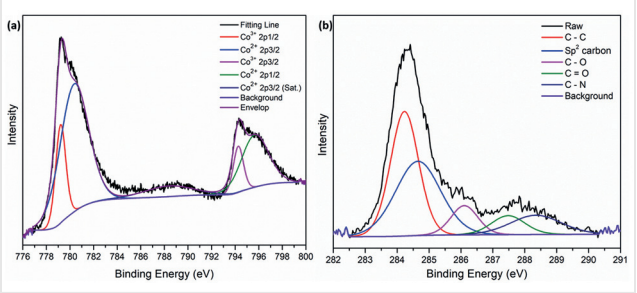


Figure 2 (a) Elemental XPS scan for Co(2p); (b) Elemental XPS scan for C(1s)

Catalytic Investigation of CoOCN for the Hydration of Alkynes. In the past decade, cobalt complexes have been extensively used for alkyne hydrations.[43] Co(III) in its various complex forms has been reported as a potential catalyst for the hydrations of alkynes.[43,44] However, all of these methods are promising but quite expensive. We initiated trials of reactions to perform such transformations by using the prepared CoOCN catalyst (Table 1).

To our delight, the use of 20 mg of CoOCN catalyst with phenylacetylene in aqueous methanol under reflux conditions produces an exceptional yield of the acetophenone. The control reaction in the absence of a catalyst does not yield any chemical change; however, the catalyst precursor $Co(NO_3)_2$ leads to 18% conversion of the desired product (Table 1, entries 1 and 3). The low yield with $Co(NO_3)_2$ could be a result of the very weak catalytic activity of Co(II), because the literature suggests that Co(III) is a more active catalyst for alkyne hydration.[45] The yield changes with a change in the quantity of catalyst to a certain extent: when the reaction was performed with 5 mg of Co catalyst, the desired product was barely observed on the TLC, whereas with 10 mg a considerable yield of 25% is produced (Table 1, entries 4 and 5). The yield of acetophenone was further improved with 15 mg of catalyst and reaches the maximum of 86% when 20 mg of catalyst was used for the transformation. A further increase in the catalyst amount does not show any substantial effects on the product yield (Table 1, entries 7 and 8). In analyzing the optimum temperature range to conduct the hydration reaction, observations were made under low-temperature conditions, close to room temperature, but unfortunately these conditions did not bring about any chemical changes. The initial traceable yield of acetophenone was first recorded at 80 °C (Table 1, entries 9 and 10). Moreover, above 80 °C, the reactions show a continuous rise in the yield of acetophenone: 20% and 39% yields of acetophenone were obtained at 90 °C and 100 °C, respectively.

Table 1 Optimization for Alkyne Hydration Reactions[a]

Entry	Catalyst	Cat. Amt. (mg)	Temp. (°C)	Time (h)	Yield[b] (%)
1	$Co(NO_3)_2$	20	120	12	18
2	CoOCN	20	120	12	86
3	–	–	120	12	–
4	CoOCN	5	120	12	trace
5	CoOCN	10	120	12	25
6	CoOCN	15	120	12	65
7	CoOCN	20	120	12	86
8	CoOCN	25	120	12	86
9	CoOCN	20	rt	12	–
10	CoOCN	20	80	12	12
11	CoOCN	20	90	12	20
12	CoOCN	20	100	12	39
13	CoOCN	20	110	12	65
14	CoOCN	20	120	12	86
15	CoOCN	20	130	12	87
16	CoOCN	20	120	4	–
17	CoOCN	20	120	6	trace
18	CoOCN	20	120	8	30
19	CoOCN	20	120	10	70
20	CoOCN	20	120	12	85
21	CoOCN	20	120	14	87

[a] *Optimized conditions*: Phenyl acetylene (1 mmol), CoOCN catalyst (20 mg, (6 mol% Co)), MeOH:H_2O (3:2), 120 °C, 12 h.
[b] Isolated yields.

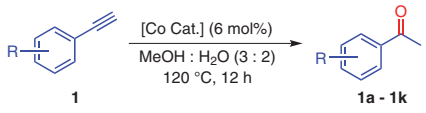
A progressive increase in the yield was recorded with a further rise in the temperature, a maximum 86% yield of the acetophenone was recorded at 120 °C, and no further change in the yield of desired product was experienced beyond 120 °C. Furthermore, to optimize the time duration of the present transformation, it was noted that the initial 6 h of the reaction yield only a trace of the desired product, whereas 30% product was formed in 8h, and the yield was further increased to 70% in next 2 h. Significant transformations of 85% and 87% were recorded in continuous 10 and 12 h reactions, respectively. No substantial changes were observed upon further escalating the reaction time of the present transformations.

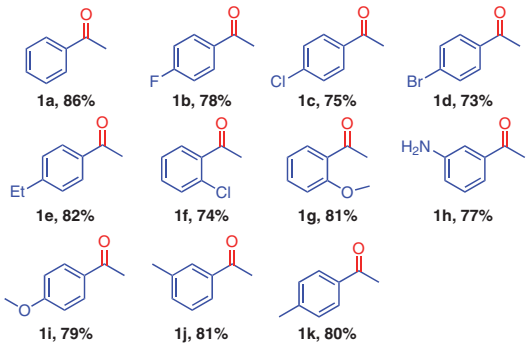
After establishing the most suitable optimized conditions, the next step is to investigate the scope of the reaction for various functionalized aryl acetylenes (Table 2). During our investigations, it was observed that both electron-withdrawing and -donating functional groups react in a similar fashion and significantly yield the desired products. However, a slightly better yield was obtained when electron-donor functionalities were present on the aryl ring. Halides (F, Cl, and Br) present at the *para* position of the aryl ring react smoothly and produce excellent yields of 78%, 75%, and 73% (Table 2, 1b, 1c, and **1d**), respectively. A slight increase in the yield to 82% was recorded with *para*-ethylphenylacetylene (Table 2, 1e). Moreover, moving on to the different positions on the aryl ring, a slight variation was experienced: chloride and methoxy groups present on the *ortho* position of phenylacetylene yield 74% and 81% (Table 2, 1f and **1g**), whereas *meta*-substituted 3-aminophenylacetylene produces a 77% yield of the corresponding ketone (Table 2, 1h). Yields of 79% and 81% were recorded for *para*-methoxy- and *meta*-methylphenylacetylene, respectively (Table 2, 1i and **1j**). Apart from that, the *para*-tolylacetylene shows an excellent conversion to give 80% of the corresponding product (Table 2, 1k).

Catalytic Investigation of CoOCN for Nitrile Hydration. The catalytic scope of the composite was further extended for the hydration of nitriles. The literature states that a variety of metal oxides, including Co_3O_4, are known to facilitate nitrile hydration.[39] However, most of the catalysts need a high temperature and may lead to over hydrolysis of desired products.[39] It was noted that the reaction worked significantly under the same optimized parameters that were adopted for alkyne hydrations (Table 3). The initial reaction with benzonitrile shows an excellent transformation to benzamide, and an 87% yield was recorded (Table 3, 2a).

para-Substituted halides (Cl, Br, and I) of benzonitriles efficiently participated in the reaction and produced 84%, 81%, and 79% yields of the corresponding amide products (Table 3, 2b, 2c, and **2d**). The reaction of *ortho*-chlorobenzonitrile yields 82% of the desired product (Table 3, 2f). The *ortho*- and *para*-methyl-substituted benzonitriles were also transformed into the corresponding nitriles with 83% and

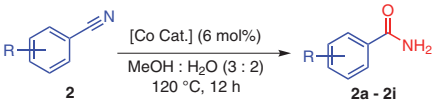
Table 2 Substrate Scope for Alkyne Hydration Reactions[a]

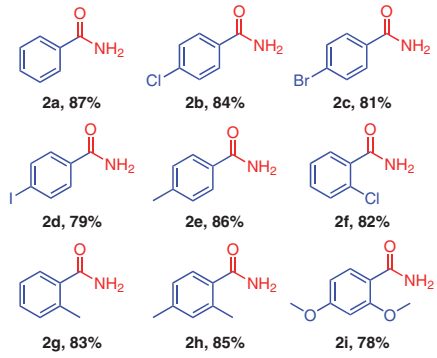




[a] *Reaction conditions*: Alkyne (1 mmol), Co catalyst (6 mol%), MeOH:H_2O (3:2), 120 °C, 12 h. Isolated yields.

Table 3 Substrate Scope for Nitrile Hydration Reactions[a]





[a] *Reaction conditions*: Benzonitrile (1 mmol), Co catalyst (6 mol%), MeOH:H_2O (3:2), 120 °C, 12 h. Isolated yields.

86% yields, respectively (Table 3, 2e and **2g**). Disubstituted benzonitriles were also checked for the hydrations, and significant transformations of the desired products were experienced: 2,4-dimethyl-, and 2,4-dimethoxybenzonitrile produced 85% and 78% yields of the desired amide products (Table 3, 2h and **2i**).

Catalytic Investigations of CoOCN for the Reduction of Nitrobenzene. Encouraged by the excellent results obtained for alkynes and nitrile hydration reactions, we further extended the catalytic potential of CoOCN for the reduction of ni-

tro compounds (Table 4). The trial reaction of nitrobenzene led to excellent transformation of the aniline in the catalytic present of CoOCN with hydrazine hydrate as the source of hydrogen and water as the solvent. To optimize the reaction conditions, the reaction of nitrobenzene was chosen as a model reaction and the effects of various parameters were studied, such as in situ H source, solvent, temperature, and time under aerobic conditions.

Table 4 Optimization of Various Reaction Parameters for the Nitro Reduction of Nitrobenzene[a]

Entry	Co Cat. (mg)	H Source	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	–	$N_2H_4{\cdot}2H_2O$	H_2O	100	12	ND
2	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	5	80
3	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	5	70
4	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	5	60
5	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	5	ND
6	20	$CH_3COOH + Et_3N$	H_2O	100	5	ND
7	20	$HCOOH + Et_3N$	H_2O	100	5	ND
8	20	IPA+KOH	H_2O	100	5	ND
9	20	$N_2H_4{\cdot}2H_2O$	MeOH	100	5	52
10	20	$N_2H_4{\cdot}2H_2O$	EtOH	100	5	50
11	20	$N_2H_4{\cdot}2H_2O$	*i*PrOH	100	5	47
12	20	$N_2H_4{\cdot}2H_2O$	H_2O	rt	5	ND
13	15	$N_2H_4{\cdot}2H_2O$	H_2O	60	5	ND
14	10	$N_2H_4{\cdot}2H_2O$	H_2O	80	5	50
15	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	5	84
16	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	1	trace
17	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	2	31
18	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	4	53
19	20	$N_2H_4{\cdot}2H_2O$	H_2O	100	8	80

[a] *Reaction conditions*: Nitrobenzene (1 mmol), $N_2H_4{\cdot}2H_2O$ (2 mmol), CoOCN catalyst (20 mg, (6 mol% Co)). ND: Not detected.
[b] Isolated Yields.

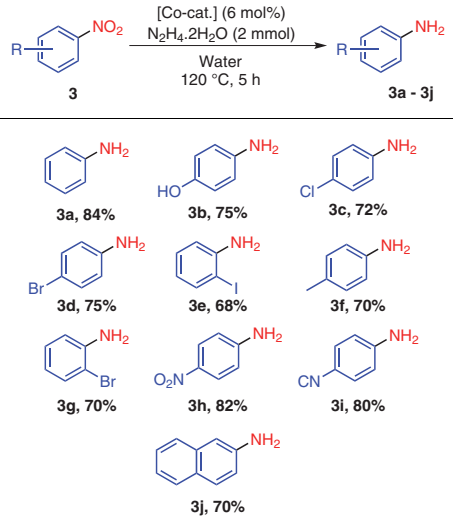
It is observed that hydrazine hydrate acts as a better hydrogen source than other combinations. The reactions at various temperatures were also studied, and it was found that 80 °C temperatures result in 50% conversion, whereas increasing the temperature to 100 °C significantly improved the yield to 81%. Further increasing the temperature did not show any significant effect on the yield or reaction time. For the assurance of the optimal catalytic amount, we carried out a blank test, in which no transformation was observed. The reaction gave product when 10 mg of catalyst was utilized. Further amplification in the yield of the product was obtained when 20 mg of catalyst was used. However, no further increase in yield was noticed with 25 mg of catalyst. Therefore, the desired results were obtained with 20 mg of catalyst. To verify the solvent effects in the reduction of nitroarenes, a series of reactions were performed by performing the model reaction in different solvents. The reaction conducted in the greener solvent water was found to be most effective. The use of other polar solvents, like isopropanol alcohol, ethanol, and methanol, leads to a decreased yield of product.

Literature about nitro reductions indicates the dual reduction of nitrobenzenes containing halogen derivatives, in which, as well as nitro group reduction, dehalogenation also takes place. Various research groups and industries are engaged in the search for and development of selective reduction processes for halogen-substituted nitrobenzene, which highlights the importance of this transformation.

Hence, to examine the scope of nitro reduction, various substituted nitro arenes, along with conventional halogen-substituted nitroarenes, mostly containing C–Br and C–I, were investigated because iodo-substituted nitro arenes are more susceptible to hydro-halogenation than Br, Cl, and F derivatives. Table 5 shows the substrate scope of the nitro reduction reactions. The initial reactions of nitrobenzene yield the highest outcome and produce 84% transformation of the aniline (Table 5, 3a). Furthermore, the *para*-hydroxy-, *para*-chloro-, and *para*-bromonitrobenzenes were also investigated for the present transformation, and 75%, 72%, and 75% yields of the respective products were recorded (Table 5, 3b, 3c, and **3d**). However, during the investigation of *ortho*-substituted halides of nitrobenzene, a slightly reduced trend of reactivity was observed, and 68% and 70% transformations was recorded with the iodo and bromo derivatives of nitrobenzene (Table 5, 3e and **3g**). It was quite surprising, because it was in contrast to available reports, that the present reaction selectively reduced only the nitro group, whereas the halide was intact during the reaction. A comparison of the yields of *para*-tolylnitrobenzene with 1,4-dinitrobenzene and *para*-cyanonitrobenzene clearly indicates that the reaction favors the presence of electron-withdrawing functionalities: *para*-tolylnitrobenzene shows 70% transformation, whereas 82% and 80% yields were recorded with the other two reactants (Table 5, 3f, 3h, and **3i**). A 70% yield was recorded for a reaction with 2-nitronapthalene (Table 5, 3j).

Reusability and Recyclability of the CoOCN Catalyst for Hydration and Reduction Reactions. The catalyst was found to be robust, reusable, and not deactivated much up to several catalytic cycles, even after use in high-temperature conditions (Figure 3). For nitrile hydration, the CoOCN composite worked for up to seven cycles, and the activity of the catalyst was almost the same during the initial three cycles. In the case of alkyne hydration, the catalyst was found to be active up to the fifth cycle. Reasonably consistent results were observed until the fourth catalytic cycle, and a sudden drop in percentage transformation was recorded in the fifth catalytic cycle: 41% of acetophenone was isolated. A similar

Table 5 Substrate Scope for Nitro Reduction[a]



[a] *Reaction conditions*: Nitroarene (1 mmol), $N_2H_4{\cdot}2H_2O$ (2 mmol), Co catalyst (6 mol%), water, 100 °C, 5 h. Isolated yields.

trend in the catalytic activity was observed for the nitrile hydration: up to four cycles, a substantial yield of amide was recorded, and the next three cycles showed a slightly reduced transformation of the desired product, because 43% yield was recorded in the seventh cycle. To reuse the catalyst, no activation or any other pretreatment was required for recharging the catalyst. The reusability of the catalyst for nitro reductions was also investigated, and it was found to be similar to that for the hydration reactions. The activity of the catalyst dropped from 84% to 48% during seven consecutive catalytic cycles.

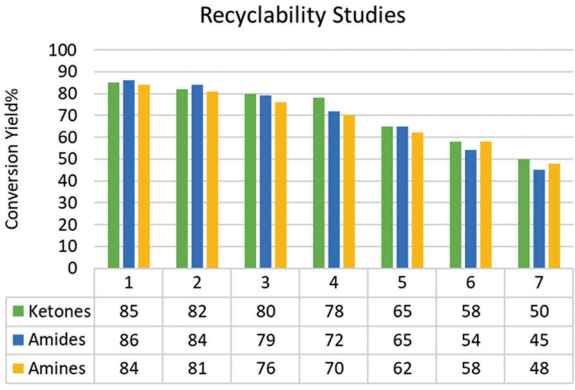


Figure 3 Recyclability test for alkyne hydrations, nitrile hydrations, and nitro reductions

In conclusion, a CoOCN composite was synthesized, characterized, and utilized as a heterogeneous catalyst for the hydration of aryl alkynes and nitriles to form the respective ketones and amides. The prepared catalyst was also used for the nitro reduction reaction in a similar optimized reaction by using hydrazine hydrate as an in situ hydrogen source. The optimized reaction conditions show sizable transformations to produce all of the products in good to very good amounts; the catalyst was found to be compatible with a wide range of functionalities. All reactions were performed under aerobic conditions, and aqueous methanol was used as the solvent. The prepared catalyst is highly stable, efficient, economical, reusable up to seven catalytic cycles, easy to synthesize, and easy to separate from the reaction mixture. The methodology has the advantage to be useful for the bulk synthesis of ketones. The applicability of CoOCN for the three different reactions reflects the massive catalytic potential of this heterogeneous catalyst, and it can serve as an ideal catalyst to meet the industrial requirements for large-scale transformations.

Reactants, reagents, chemicals, and solvents available commercially within the country were used. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded by using a JEOL ECS-400 spectrometer (operating at 400 MHz for ^1H and 101 MHz for ^{13}C).

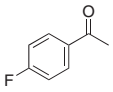
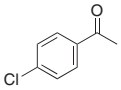
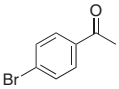
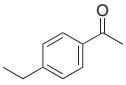
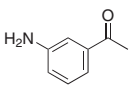
Alkyne or Nitrile Hydration Reactions; General Procedure

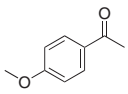
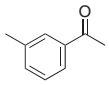
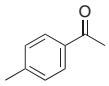
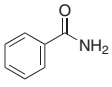
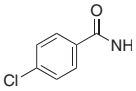
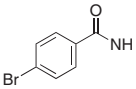
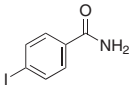
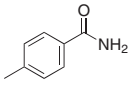
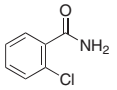
The desired aryl alkyne or aryl nitrile (1 mmol) in a mixture of MeOH and H_2O (3:2, MeOH (1 mL), H_2O (0.66 mL)) was placed in a reaction tube, CoOCN catalyst (20 mg, 6 mol% Co) was added, and the reaction mixture was stirred for 12 h at 120 °C. After completion of the reaction, the catalyst was separated by filtration and the product was extracted by solvent extraction with ethyl acetate. The extracted solvent was dried over anhydrous Na_2SO_4, concentrated at reduced pressure, and purified by flash column chromatography with hexanes/ethyl acetate as the eluent to obtain the corresponding product.

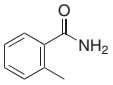
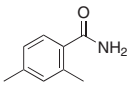
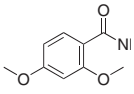
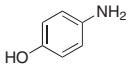
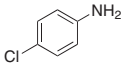
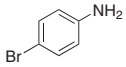
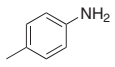
Nitro Reduction Reaction; General Procedure

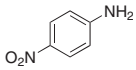
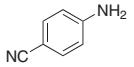
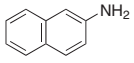
Nitro aryl (1 mmol) was placed in a reaction tube, then add $N_2H_4{\cdot}2H_2O$ (2 mmol) and CoOCN catalyst (20 mg, 6 mol% Co) were added, and the reaction mixture was stirred for 12 h at 120 °C with water (1.5 mL) as the solvent. After completion of the reaction, the catalyst was separated by filtration and the product was extracted by solvent extraction with ethyl acetate. The extracted solvent was dried over anhydrous Na_2SO_4, concentrated at reduced pressure, and purified by flash column chromatography with hexanes/ethyl acetate as the eluent to obtain the corresponding anilines.

Table 6 NMR Data for Products

Product	Compound number, name, NMR data
	**1a**, acetophenone[46] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.1, 0.9 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 2.59 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.84, 136.80, 132.80, 128.26, 127.99, 26.29.
	**1b**, 4-fluoroacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 8.8, 5.5 Hz, 2 H), 7.13 (t, *J* = 8.6 Hz, 2 H), 2.59 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.67, 167.21, 164.67, 133.76 (d, *J* = 2.7 Hz), 131.13 (d, *J* = 9.4 Hz), 115.94, 115.72, 26.71.
	**1c**, 4-chloroacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.70 (m, 2 H), 7.31–7.24 (m, 2 H), 2.45 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.73, 138.47, 134.43, 128.75, 127.86, 25.53.
	**1d**, 4-bromoacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.72 (m, 2 H), 7.57–7.50 (m, 2 H), 2.52 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.71, 135.50, 131.58, 129.53, 128.00, 26.24.
	**1e**, 4-ethylacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 2.70 (q, *J* = 7.6 Hz, 2 H), 2.57 (s, 3 H), 1.25 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.75, 149.94, 134.81, 128.44, 127.96, 28.83, 26.43, 15.11.
	**1f**, 2-chloroacetophenone ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 1 H), 7.30–7.21 (m, 2 H), 7.21–7.15 (m, 1 H), 2.50 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.56, 138.35, 131.34, 130.50, 129.94, 128.72, 126.29, 29.96.
	**1g**, 2-methoxyacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.7, 1.8 Hz, 1 H), 7.46 (ddd, *J* = 8.4, 7.4, 1.9 Hz, 1 H), 7.10–6.93 (m, 2 H), 3.90 (s, 3 H), 2.61 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.03, 159.10, 133.87, 130.49, 128.39, 120.69, 111.77, 55.64, 32.01.
	**1h**, 3-aminoacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 7.7, 0.9 Hz, 1 H), 7.25 (dt, *J* = 15.6, 4.9 Hz, 2 H), 6.97–6.84 (m, 1 H), 3.68 (s, 2 H), 2.56 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.70, 146.91, 138.44, 129.67, 119.90, 119.13, 114.24, 26.95.

Product	Compound number, name, NMR data
	**1i**, 4-methoxyacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.8, 0.8 Hz, 2 H), 7.00–6.91 (m, 2 H), 3.88 (s, 3 H), 2.57 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.84, 163.55, 130.65, 113.74, 55.52, 26.40.
	**1j**, 3-methylacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.69 (m, 2 H), 7.34 (m, *J* = 7.6 Hz, 2 H), 2.57 (s, 3 H), 2.39 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.34, 138.35, 137.17, 133.89, 128.81, 128.48, 125.62, 26.67, 21.34.
	**1k**, 4-methylacetophenone[47] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 2.58 (s, 3 H), 2.41 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.56, 143.58, 134.41, 128.94, 128.14, 26.23, 21.33.
	**2a**, benzamide[45] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.73 (m, 2 H), 7.54–7.47 (m, 1 H), 7.46–7.38 (m, 2 H), 6.29 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.41, 133.05, 131.68, 128.31, 127.02.
	**2b**, 4-chlorobenzamide[45] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.6 Hz, 2 H), 7.95 (d, *J* = 8.6 Hz, 2 H), 5.94 (d, *J* = 128.8 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.30, 149.60, 139.52, 128.97, 123.51.
	**2c**, 4-bromobenzamide[48] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.57 (m, 2 H), 7.53 (dd, *J* = 8.6, 1.8 Hz, 2 H), 5.83 (d, *J* = 115.8 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.43, 132.10, 129.15, 127.04, 124.09.
	**2d**, 4-iodobenzamide[48] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 5.77 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.55, 138.13, 133.36, 129.12, 99.31
	**2e**, 4-methylbenzamide[45] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.65 (m, 2 H), 7.27–7.18 (m, 2 H), 5.95 (s, 2 H), 2.39 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.41, 142.53, 130.66, 129.31, 127.44, 21.49.
	**2f**, 2-chlorobenzamide[45] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 7.5, 1.6 Hz, 1 H), 7.40–7.21 (m, 3 H), 6.34 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.35, 133.88, 131.90, 130.71, 130.48, 127.24, 100.00.

Product	Compound number, name, NMR data
	**2g**, 2-methylbenzamide[45] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.31–7.18 (m, 2 H), 6.05 (d, *J* = 141.0 Hz, 2 H), 2.51 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.31, 136.40, 135.27, 131.30, 130.37, 127.03, 125.83, 20.07.
	**2h**, 2,4-dimethylbenzamide ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 7.7 Hz, 1 H), 7.06–6.86 (m, 2 H), 5.80 (d, *J* = 66.8 Hz, 2 H), 2.40 (s, 3 H), 2.26 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.13, 140.62, 136.66, 132.16, 127.26, 126.44, 21.34, 20.17.
	**2i**, 2,4-dimethoxybenzamide ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.8 Hz, 1 H), 7.58 (s, 1 H), 6.55 (dd, *J* = 8.8, 2.3 Hz, 1 H), 6.44 (d, *J* = 2.2 Hz, 1 H), 6.28 (s, 1 H), 3.88 (s, 3 H), 3.81 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.21, 163.90, 159.30, 134.21, 113.88, 105.32, 98.59, 55.78.
	**3a**, aniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.09 (m, 2 H), 6.72 (t, 1 H), 6.66–6.64 (m, 2 H), 3.37 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.27, 129.35, 118.70, 115.22.
	**3b**, 4-hydroxyaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92–6.84 (m, 2 H), 6.72–6.70 (m, 2 H), 6.60 (s, 1 H), 6.55 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.74, 141.17, 116.05, 115.75.
	**3c**, 4-chloroaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.03 (m, 2 H), 6.56–6.53 (m, 2 H), 3.55 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.06, 129.18, 123.15, 116.32.
	**3d**, 4-bromoaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.16 (d, 2 H), 6.49 (d, 2 H), 3.52 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.47, 132.06, 116.77, 110.23.
	**3e**, 2-iodoaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 1 H), 7.10–7.08 (m, 1 H), 6.72–6.70 (m, 1 H), 6.45–6.41 (m, 1 H), 3.99 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.79, 139.04, 129.39, 120.03, 114.78, 84.22.
	**3f**, 4-methylaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (d, 2 H), 6.57 (d, 2 H), 3.42 (s, 2 H), 2.21 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.89, 129.84, 127.85, 115.35, 20.54.

Product	Compound number, name, NMR data
	**3g**, 2-bromoaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 1 H), 7.07–7.03 (m, 1 H), 6.73–6.71 (m, 1 H), 6.59–6.54 (m, 1 H), 3.96 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.10, 132.63, 128.38, 119.46, 115.79, 109.37.
	**3h**, 4-nitroaniline[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, 2 H), 6.59 (d, 2 H), 4.36 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6, 139.2, 126.4, 113.4.
	**3i**, 4-cyanobenzonitrile[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, 2 H), 6.60 (d, 2 H), 4.18 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.6, 133.9, 120.3, 114.5, 100.0.
	**3j**, naphthalen-2-amine[12c] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.62 (m, 2 H), 7.47–7.14 (m, 4 H), 6.71 (d, *J* = 6.9 Hz, 1 H), 3.99 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.1, 134.5, 128.6, 126.4, 125.9, 124.9, 123.7, 120.9, 119.1, 109.8.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-2025-2759.

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