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Chemoselective Hydrogenation of Functionalized Nitroarenes Using MOF-Derived Co-Based Catalysts

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Graphical Abstract

A novel MOF-derived metallic cobalt-based catalyst is developed for chemoselective hydrogenation of substituted nitroarenes. A broad range of substituted nitroarenes are converted to the corresponding anilines in 93-99% yields under industrially viable conditions with other reducible groups remaining intact.



Highlights

- Co/C-N was prepared by simple pyrolysis of MOFs.
- Nitroarenes are converted to anilines with other reducing groups remaining

intact.

- Co-N centers present in the catalyst lead to the unique chemoselectivity.
- The reaction showed a first-order dependence on H₂ pressure.

Abstract

The synthesis, characterization, and application of nitrogen-doped carbon supported Co catalysts in selective hydrogenation of nitroarenes are described. The cobalt-based catalysts are prepared by simple pyrolysis of ZIF-67, a typical MOF material, under inert atmosphere. Physicochemical properties of the Co/C-N catalysts have been investigated by X-ray diffraction, elemental analysis, atomic absorption spectroscopy, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The Co-based materials were found to be highly efficient in the chemoselective hydrogenation of nitroarenes. A broad range of substituted nitroarenes are converted to the corresponding anilines in excellent yields under industrially viable conditions with other reducing groups remaining intact. In situ ATR-IR and XPS characterizations reveal that the Co-N centers present in the catalyst favor the preferential adsorption of nitro groups, leading to this unique chemoselectivity. The kinetic parameters of 4-nitrostyrene hydrogenation over the Co/C-N catalyst were investigated.

Keywords: heterogeneous catalysis, cobalt, metal-organic frameworks, amines, hydrogenation

1. Introduction

Aniline and its derivatives, with more than 4 million tons produced per year, are known as major feedstocks and key intermediates for the synthesis of pharmaceuticals, dyes, functional polymers, agrochemicals, and fine chemicals [1,2].Generally, anilines are prepared by reduction of corresponding nitro substrates. However, the traditional non-catalytic processes require stoichiometric amounts of reducing agents (e.g., Fe, Sn, Zn and metal sulfides) that generate a large number of wastes [3]. Similarly, catalytic routes utilizing various reducing agents are often troubled by the violent reduction (e.g., NaBH4), toxic (e.g., N2H4•H2O), or potentially explosive (e.g., silicon hydride) issues [4-17]. As the most environmentally benign and cost-effective reducing agent, hydrogen would be the preferred choice in the catalytic reduction of nitroarenes. Nevertheless, the selective hydrogenation of a nitro group in the presence of other reducible substituents, e.g., carbonyl, cyano, benzyloxy, and alkenic groups, is challenging. Therefore, it is crucial to develop chemoselective catalysts for the reduction of nitro groups.

Noble-metal catalysts (e.g., Au, Ag, Pt, Pd, Rh, and Ru) have been deeply investigated for the catalytic hydrogenation of nitro groups [18-46]. However, the problem often arising is that the highly active noble metals can activate nitro groups as well as carbonyl and double bonds, leading to unselective reductions. It is generally accepted that commercially available Pd or Pt catalysts cannot be used to hydrogenate substituted nitrobenzenes, since the selectivity still remains low. So these catalysts must be modified by alloying or poisoning with other metal oxides or molecules that

improve selectivity but at the expense of activity [42-46]. More recently, Corma et al. approached this issue by controlling the coordination of metal surface atoms and selecting an appropriate support [18,28]. Despite high activity achieved with noble metals, the high cost and limited availability of these metals is a big issue which leads researchers to develop more economical and bio-relevant alternatives.

In this context, catalytic reductions based on non-noble metals (e.g., Fe, Co, Ni, Cu, and Zn) have been investigated intensively [47-64]. The commercially available Raney-nickel catalyst also suffers from the unselective problems mentioned above. Modification of the catalyst with B, P, Ni-B, Ni-P, or Ni-P-B have been investigated as possible means to enhance the selectivity [62-64]. Cu-based catalysts have also been found to be selective for this reaction, but these catalysts require relatively harsh reaction conditions [59]. Cobalt catalysts are scarcely utilized for this transformation [12,43,44]. Zhao et al. inserted Co into the Mo₂C matrix to promote the formation of molybdenum carbide crystal phase, achieving an improvement in reactivity for catalytic reduction of nitroarenes [12]. Raja et al. reported Co nanoparticles supported on mesoporous silica for the hydrogenation of nitroarenes [43]. High reactivity was obtained even with large-scale substrates. But the chemoselectivity over these Co catalysts was limited due to the absence of challenging substrates bearing reducible groups, e.g., olefins, and alkynes. More recently, important advancements have been reported by the group of Beller, who disclosed heterogeneous catalytic systems based on carbonized cobalt- or iron-phenanthroline complexes that displayed exciting selectivity for numerous structurally diverse nitroarenes [47,50]. However, the

catalysts require relatively expensive nitrogen-containing precursors as well as high H₂ pressure (50 bar). Therefore, the development an efficient and cost-effective non-noble metal catalyst system for chemoselective reduction of all kinds of nitroarenes is highly desirable.

Metal-organic frameworks (MOFs) are an emerging class of ordered porous materials built with metal ions and organic ligands. Recently, thermal decomposition of MOFs has been demonstrated as a facile route to synthesize metal containing porous carbon materials [65-68]. In our previous study, we demonstrated that pyrolysis of a cobalt-containing MOF yielded highly dispersed metallic Co nanoparticles embedded in N-doped carbon (Co/C-N) [69]. The excellent redox property of Co-based materials drove us to explore the catalytic activity of Co/C-N for the hydrogenation of nitroarenes. Here, we show that these MOF-derived materials represent excellent catalysts for the chemoselective hydrogenation of a variety of functionalized nitroarenes to anilines with other reducible groups untouched. The superior catalytic performance can be attributed to the presence of Co-N centers which favor preferential adsorption of the nitro groups. Moreover, these Co-based catalysts are easily separated and can be conveniently reutilized, which is an important aspect in the development of practical and cost-effective catalytic hydrogenation processes.

2. Experimental Section

 $Co(NO_3)_2 \cdot 6H_2O$ (A.R.), methanol (A.R.), ethanol (A.R.), DMF (A.R.), THF (A.R.), ethyl acetate (A.R.), and isopropyl alcohol (A.R.) were purchased from the Sinopharm Chemical Reagent Co., Ltd. 2-Methylimidazole (98%),

1,4-benzenedicarboxylic acid (98%), polyvinylpyrrolidone (PVP, M.W. = 30000), NaBH₄ (98%), and nitroarenes (>99%) were purchased from Alfa Aesar. Commercial samples of 5% Pd, Pt, Ru, and Rh on active charcoal and pure active charcoal were purchased from Sigma-Aldrich. Deionized water with conductivity <1 μ S/cm was obtained from the ultrapure water polishing system made by Shanghai Xunhui Environment Technology Co., Ltd. All chemicals were used without further purification.

2.1. Materials preparation

In a typical synthesis of ZIF-67 [69], cobalt nitrate hexahydrate (0.45 g, 1.55 mmol) was dissolved in 3 mL of deionized water (0.52 mol/L), and 2-methylimidazole (5.5 g, 67 mmol) was dissolved in 20 mL of deionized water (3.35 mol/L). The two solutions were mixed and stirred for 6 h at room temperature. The resulting purple precipitates were collected by centrifugation and filtration, washed with water and methanol subsequently for 3 times, and finally dried under vacuum at 80 °C for 24 h. In the synthesis of Co-MOF-71 [70], a solid mixture of Co(NO₃)₂•6H₂O (0.4 g, 1.37 mmol) and 1,4-benzenedicarboxylic acid (230 mg, 1.37 mmol) was dissolved in a single binary solution of DMF (10 mL) and ethanol (2.5 mL). The resulting solution was transferred into a Pyrex tube, frozen in a liquid N₂

bath, evacuated (200 mTorr), flame-sealed and then heated at 100 °C for 15 h. The resulting pink/purple crystals of Co-MOF-71 were collected by filtration, washed with DMF subsequently for 3 times, and finally dried overnight under vacuum at 150 °C.

Co/C-N catalyst was synthesized by direct pyrolysis of ZIF-67 (Yield, ca. 60 wt%). In a typical preparation, 1 g of pre-synthesized ZIF-67 was pyrolyzed at a particular temperature for 10 h with a heating rate of 1 °C/min under argon atmosphere. The prepared catalyst was denoted as Co/C-N-X, where X indicated the MOF pyrolysis temperature. Co/C-X was prepared following the same procedures as above except using Co-MOF-71 as sacrificed templet.

For comparison, an activated carbon (Sigma-Aldrich) supported metallic Co sample was also prepared by using a simple colloidal deposition method [71]. Firstly, 10 mL aqueous solution of Co(NO₃)₂•6H₂O (740 mg, 2.54 mmol) was prepared, and PVP (2.82 g, 25.4 mmol) was added as a protecting agent. The obtained solution was placed in an ice bath and vigorously stirred for 1 h. 5 mL freshly prepared aqueous solution of NaBH₄ (96 mg, 2.54 mmol) was added under vigorous stirring to obtain a dark brown colloidal dispersion. The preformed Co:PVP hydrosol was subjected to sonication for 20 s, and during the sonication, 10 mL aqueous solution of activated carbon (500 mg) was added. The suspension was stirred at 0 °C for 4 h, followed by washing thoroughly with deionized water. The powder was dried under vacuum at 100 °C for 2 h and then heated at 200 °C in H₂ for 2 h to obtain the Co/C. Ni/C was also prepared by the same recipe except using Ni(NO₃)₂•6H₂O as the metal precursor.

2.2. Materials characterization

Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) employing Cu K α radiation ($\lambda = 0.1543$ nm) at 40 kV, 30 mA at room temperature. 2θ scans were performed from 20° to 100° at 3°/min. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10⁻⁹ Torr. The size and morphology of materials were investigated by high-resolution scanning electron microscopy (HR-SEM, S-3700N of HITACHI) equipped with an energy dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HR-TEM, C/M300 of Philips) operated at 30 kV and 200 kV respectively.

2.3. General procedure for hydrogenation

The hydrogenation of nitroarenes was carried out in a Teflon-lined stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer. Typically, a mixture of 0.5 mmol nitroarene, 15 mol% Co/C-N-X catalyst, 100 μ L *n*-hexadecane and 2 mL solvent was introduced into the reactor at room temperature. Air in the autoclave was purged several times with H₂. Then, the reaction began by starting the agitation (600 r/min) when hydrogen was regulated to 1 MPa after the reaction temperature was reached. After reaction, the solid was isolated from the solution by centrifugation. The products in the solution were quantified and identified by GC-MS analysis (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary column). ¹H NMR and ¹³C NMR data were obtained on Bruker Avance III 400 spectrometer using

CDCl₃ or DMSO-d6 as solvent and tetrmethylsilane (TMS) as an internal standard. The pure product in the scale-up experiment was obtained by flash column chromatography (petroleum ether and ethyl acetate).

For the recyclability test, the reactions were performed maintaining the same reaction conditions as described above, except using the recovered catalyst. At the end of catalytic reaction, the mixture was centrifuged and the solid was recovered, which was thoroughly washed with methanol, and then reused in a next run.

To determine whether there was any leaching of Co during the reaction, the solid catalyst was removed from the reaction solution by hot filtration. The metal contents of the filtered solution were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

2.4. In situ ATR-IR spectroscopy

ATR-IR spectra were recorded on a Thermo Fisher iS10 equipped with a liquid nitrogen cooled MCT detector. The spectra were obtained by averaging 32 scans at a resolution of 1 cm⁻¹. The thin film of catalyst powder deposited on the ZnSe element for ATR-IR spectroscopic study was prepared as follow. A suspension of ca. 50 mg of catalyst powder in 2 mL of methanol was stirred overnight to eliminate any serious agglomeration in solution. Then, the slurry was dropped onto a ZnSe internal reflection element (IRE) and dried out at room temperature, which was subsequently dried in a vacuum oven for a complete evaporation of methanol.

3. Results and Discussions

3.1. Optimization of reaction conditions

Nanoscale Co-based catalysts were prepared by pyrolysis of a Co-containing MOF (ZIF-67) under a typical temperature ranging from 600 °C to 900 °C.

Disappearance of obvious peaks ascribed to the characteristic diffractions of ZIF-67 in the range of 5-20 degrees (Fig. S1) suggested the complete collapse of the ordered pristine structure after the pyrolysis process. The as-synthesized nanoparticles were identified as face-centered-cubic (fcc)-structured cobalt (JCPDS 15-0806) from the powder XRD patterns, where the major diffraction peak could be indexed to the (111) diffraction plane (Fig. S2). The TEM images (Figs. 1 and S3) of Co/C-N-600 revealed an average particle size of ~9 nm in spheric shape. Typical scanning electron microscopy (SEM) images were displayed in Fig. S4. As can be seen from the corresponding elemental mapping images, Co, C, and N were homogeneously distributed in Co/C-N.

We investigated the catalytic activities of the freshly prepared nanocatalysts for the selective hydrogenation of nitro groups by using 4-nitrostyrene (denoted as NS) as a benchmark substrate. As can be seen from Table 1, the parent ZIF-67 gave no conversion of 4-nitrostyrene, suggesting that cobalt ions coordinated with 2-methylimidazole were not active for reduction of nitroarenes under the investigated conditions (entry 1). However, ZIF-67 pyrolyzed materials showed great performance in this transformation, and significantly, Co/C-N-600 exhibited the highest conversion and 97% selectivity to the target product 4-aminostyrene (Table 1, entries 2-5) under

the investigated reaction conditions. Both conversion and selectivity decreased with an increase in pyrolysis temperature of the MOF. As the nitrogen content (e.g., 12.0 wt% at 600 °C, and 3.3 wt% at 800 °C) in the Co/C-N also decreased with increasing temperature (Table S1), these results suggested the presence of nitrogen might play an important role in this catalytic system. A complete conversion could be obtained by simply prolonging reaction time without any significant reduction in product selectivity (Table 1, entry 6).

To identify the active site for 4-nitrostyrene hydrogenation, we examined the catalytic efficiency of Co/C-N-600 after removing the metallic Co or carbon under identical conditions. First, the as-synthesized Co/C-N-600 was immersed in aqua regia for 24 h, and the yielded material was denoted as Co/C-N-600-C. As illustrated in Figs. S5 and S6, after acid treatment, the Co nanoparticles were completely removed from the carbon matrix. The Co/C-N-600-C was not active in the hydrogenation of 4-nitrostyrene, demonstrating the requirement of a metal to catalyze the reaction (Table 1, entry 7). On the other hand, the Co/C-N-600 material was subjected to heating at 400 °C for 1 h in air and then for 1 h in H₂. The carbon composite was almost burned off after this treatment, and the resulting material was denoted as Co/C-N-600-Co. Co/C-N-600-Co showed poor activity and produced 4-aminostyrene in only 4% yield (Table 1, entry 8). Furthermore, we investigated the activity of Co nanoparticles supported on activated carbon (Co/C) [71]. Interestingly, this materials exhibited no reactivity (Table 1, entry 9).

In order to gain insight into the role of nitrogen in this catalytic system, we

conducted another control experiment using the material Co/C-X derived from another cobalt-containing MOF without nitrogen element (Co-MOF-71). Co/C-600 possessed the similar structure as Co/C-N-600 except the absence of N element (Figs. S3, S7 and Table S1). Interestingly, poor conversion and unsatisfactory selectivity (50%) were observed over the Co/C-600 material (Table 1, entry 10). The above control experiments suggest the important synergic interactions between the N-doped carbon composite and Co nanoparticles for the catalytic performance of Co/C-N-600 in the hydrogenation of 4-nitrostyrene. Reactions catalysed by typical supported transition-metal catalysts were also conducted (Table 1, entries 11-15). All the supported catalysts except Ni/C exhibited high activities towards the hydrogenation of 4-nitrostyrene with complete conversion under the same conditions. However, the product was 4-ethylaniline with the alkenic group hydrogenated. The selectivity to the target product 4-aminostyrene were 0%. These results are in accordance with the data reported in the literature [18,22], demonstrating the speciality of the present materials for selective hydrogenation of nitroarenes.

As the solvent strongly affects the activity and chemoselectivity of the reaction [13], the effect of solvents was also investigated. Results of the hydrogenation showed that changing the solvent indeed influenced reaction efficiency dramatically. However, no apparent change of product selectivity was observed. Reductions in protonic solvents gave better yields as compared to aprotic solvents (Table S2, entries 1-8). Taking THF as an example, only 23% conversion, which was the lowest one among the solvents we investigated, was obtained (Table S2, entry 2). It was interesting to

note that a big improvement in conversion was observed when the reaction was conducted in a mixed solvent in which only a small amount of H₂O was added (Table S2, entry 4), suggesting that H₂O, as a strong protonic solvent, might have a positive effect on the reaction. However, H₂O seemed to be unable to promote the reaction to a satisfactory conversion solely, probably due to poor solubility of the substrate in it (Table S2, entry 3). The reaction under N₂ atmosphere suggested that the reductant (H₂) was crucial for the reduction process (Table S2, entry 9).

3.2. Stability and reusability of Co/C-N-600

Recyclability is definitely significant for a heterogeneous catalytic system. Therefore, the stability and reusability of the Co/C-N-600 catalyst were investigated in the hydrogenation of 4-nitrostyrene. The catalyst could be easily recycled by centrifugation, sedimentation, or even by using a magnet due to the magnetic property of the Co-based material. The separated catalyst was washed with methanol and then reused under identical reaction conditions without decay in activity for at least 5 cycles (Fig. 2a). PXRD patterns showed that no apparent difference was observed between the fresh catalyst and the reused one up to five runs (Fig. S2). TEM images of the recycled catalyst indicated that there was no obvious change in particle shape and average size (ca. 9 nm) as compared to the fresh one (Fig. 1).

In order to demonstrate the synthetic utility of our catalyst system for potential practical application, the hydrogenation of 4-nitrostyrene was scaled-up by 10 under the investigated conditions. An excellent isolated yield of 95% could be achieved,

suggesting that Co/C-N-600 could be a practical catalyst for the reduction of nitroarenes to anilines. An important issue that can not be ignored at large-scale production of arylamines is the formation of hydroxylamines. These compounds, which are often less reactive as compared to the starting nitroarenes, are known as carcinogens and are potentially explosive at higher concentrations due to their thermal instability [48,72,73]. To our delight, no such intermediates like hydroxylamines were observed in our experiments with 4-ethylaniline as the only byproduct. Additionally, a leaching experiment was performed to further check the stability of the Co nanoparticles. The reaction with the solution after hot filtration at approximately 25% conversion essentially stopped (Fig. 2b) and no Co absorbance was observed to the detectable limits of AAS in the filtrate after reactions, strongly suggesting that metal leaching did not occur and the reaction was predominantly heterogeneous.

3.3. In situ ATR-IR spectroscopic study of single-component adsorption

To gain more in-depth information about the selective hydrogenation reaction, in situ ATR-IR spectroscopy was employed and 4-nitrostyrene was chosen as substrate to gain some molecular insight into the surface adsorption property of the catalysts. The Co/C-N-600 powder showed no absorbance, while three characteristic bands at 1116, 1418, and 1450 cm⁻¹ were observed for methanol in the range of 1050–1950 cm⁻¹ (Fig. S8). The ATR-IR spectra of pure 4-nitrostyrene in the liquid-phase and in methanol were also recorded (Fig. S9). The band at 1595 cm⁻¹ could be assigned to the stretching vibration of the conjugated C=C group. The peaks at 1511 cm⁻¹ and

1337 cm⁻¹ corresponded to -NO₂ stretching vibrationin 4-nitrostyrene.

Next, the adsorption of 4-nitrostyrene in Ar-saturated methanol on different catalysts was investigated. The Co/C-600 prepared from thermolysis of nonnitrogenous Co-MOF-71 was choosen as a reference catalyst to explore the potential role of nitrogen element in the adsorption of 4-nitrostyrene. Initially, the ATR-IR spectra of 4-nitrostyrene in Ar-saturated methanol at room temperature were obtained (Figs. 3a and 3b). Interestingly, no obvious change in intensity or position of the bands for v(C=C) and v(-NO₂) was observed after 2 h, implying a weak adsorption of 4-nitrostyrene on both catalysts under the condition.

However, when the temperature was elevated to 100 °C, apparent changes in peak intensity were observed, implying a chemical adsorption character. It was worth mentioning that the adsorption rates in the ATR-IR experiments were obviously slower than that obtained in a batch reactor, likely due to the mass-transfer restriction without stirring. The spectra of adsorbed 4-nitrostyrene on both Co/C-N-600 and Co/C-600 at different time are displayed in Figs. 3c and 3d. For Co/C-N-600, the band at 1595 cm⁻¹ related to C=C stretching vibrations of both the phenyl group and the conjugated C=C bond in 4-nitrostyrene, showed no obvious change in intensity or band shift with reaction time. Comparably, the characteristic absorption at 1511 cm⁻¹ and 1337 cm⁻¹ for the -NO₂ stretching vibration of 4-nitrostyrene gradually became weaker and slightly blue-shifted (by ca. 6 cm⁻¹ and 7 cm⁻¹ respectively). The above observation suggested that 4-nitrostyrene might adsorb vertically on the Co(111) surface via only the nitro group[74-76].

Thus, selective reduction of the nitro group was expected under the hydrogenation condition. However, for Co/C-600, the characteristic absorption intensities for both olefin and nitro groups decreased with time, implying 4-nitrostyrene might adsorb parallelly onto the Co(111) surface of Co/C-600 by the two groups, leading to simultaneous reduction of both groups in the hydrogenation. These results demonstrated that nitrogen played an important role in the selective adsorption of nitro group onto the catalyst surface.

This speculation was further confirmed by the XPS characterization. XPS investigations on the bonding of cobalt and nitrogen were carried out. Two distinct peaks were observed in the N 1s spectra (Fig. 4a) of Co/C-N-600 with an electron-binding energy of 399.0 eV and 401.1 eV, respectively. The peak at 399.0 eV (purple line) could be assigned to pyridinic nitrogen coordinated to cobalt [77]. The latter (red line) could be attributed to a pyrrole-type nitrogen doped into the carbon matrix [78]. Deconvolution revealed that about 67% of all nitrogen atoms were bonded to Co. Statistically, around 1.7 nitrogen atoms were coordinated to one surface cobalt atom. Carbon atoms could also bond to Co, thus the surface of an individual Co nanoparticle could be a mixture of partial cobalt nitride and partial cobalt carbide.

The contribution of electrons from nitrogen to cobalt might have a major influence on the chemical environments of Co and N in the near-surface region. Consequently, we compared the Co 2p spectra of Co/C-N-600 with Co/C-600. As can be seen from Fig. 4b, in Co/C-600, three peaks were observed at 779.3 eV (red line),

780.1 eV (blue line), and 781.6 eV (purple line) that could be ascribed to Co^0 , Co^{2+} and Co-OH species, respectively [79]. However, in Co/C-N-600, these peaks were shifted to lower binding energies (i.e., 778.7 eV, 779.7 eV, and 781.0 eV). These results suggested that the Co-N centers formed in the ZIF-67 pyrolysis process (Fig. S10), in which the Co and N atoms were tightly bonded enabling an adjustment of the electron distribution on the catalyst surface, played a critical role in the selective adsorption and hydrogenation of nitroarenes. It is notworthy that there could be a small fraction of surface Co not in contact with N because the reaction results indicated that the selectivity to 4-aminostyrene was not 100%. However, as shown in Table 1 (entries 9-10), such Co species showed a low activity under the investigated conditions. Therefore, these Co atoms not in contact with N should not be dominant because of the low fraction and reactivity. The Co nanoparticles were partially coated and isolated by the carbon support, which was believed to play an important role in preventing metal aggregation during catalytic reactions and hence enhancing the catalyst stability. Beller and co-workers first developed this kind of Co(Fe)-N-C for fine chemical synthesis, and they claimed that the Co_xO_y particles or FeN_x species in the size range of 20-80 nm were responsible for the excellent catalytic performances. More recently, Zhang et al. proposed Co single atoms bonded with N within graphitic sheets to be active sites in the Co-N-C catalyst for C-C coupling reactions [80]. However, the high cobalt loading and long calcination time would eliminate the existence of Co single atoms on the surface of our catalysts.

3.4.Effect of kinetic parameters on the catalytic performance of Co/C-N

Since the stirring speed could play an important role in the external mass transfer of a liquid-phase catalytic reaction and might affect the reaction rate and product selectivity, the hydrogenation of 4-nitrostyrene (NS) over the Co/C-N-600 catalyst was carried out under identical conditions (i.e., 1 MPa H₂, 100 °C, and 2 h), except using different stirring rates. As shown in Fig. S11, the conversion of NS increased when the stirring speed was enhanced from 400 rpm to 600 rpm. Further increaseing the stirring rate, there was no obvious improvement of NS conversion, indicating that the stirring speed was sufficiently high for negligible diffusion limitation. Therefore, the stirring rate of 600 rpm was chosen for all the hydrogenation reactions in this work.

Kinetic experiments were carried out over the Co/C-N-600 catalyst under the same conditions (i.e., 1 MPa H₂, and 100 °C), except for the initial NS concentration. Four different initial NS concentrations were investigated, i.e., 0.05, 0.15, 0.25, and 0.35 M, respectively. It can be seen from Fig. S12a that the initial NS concentration ($C_{NS,0}$) seemed to have no influence on the reaction rate. Neither did on the product distribution during the overall reaction process. To rule out the dependence of the reaction on NS concentrations, the reaction rate (r_0) at each initial concentration was determined from the concentrations versus time curves. Plot of lgr_0 versus $lgC_{NS,0}$ confirmed our former observation (Fig. S12b). The slope of the straight line for the four NS concentrations was about zero. This result suggested that the reaction would be zero-order dependence on NS concentrations.

In another set of experiments, the effect of H₂ pressure on the hydrogenation performance was investigated by varying the H₂ pressures over the range of 0.6-1.2 MPa. As can be seen in Fig. S13a, increasing the H₂ pressure enhanced the reaction rate, while the selectivity to 4-aminostyrene was still maintained at >96% for each run up to complete conversion of NS. It is plausible that a high pressure could improve the solubility of hydrogen in the reaction solution, rendering more hydrogen molecules accessible to the catalyst surface.

Plot of $\lg r_0$ against $\lg P_{H2}$ with the initial reaction rates determined from the time evolution of NS concentration for each run is presented in Fig. S13b. The fitting data indicated that $\lg r_0$ was a good linear function of $\lg P_{H2}$ with a slope of ca. 1.02, suggesting that the reaction order with respect to H₂ pressure was first-order.

The effect of reaction temperature on the catalytic hydrogenation was investigated at various temperatures in the range of 60-120 °C under 1 MPa H₂. The results are summarized in Fig. 5a. As expected, increasing the reaction temperature from 60 °C to 120 °C led to continuous shortening of reaction time for complete conversion of NS. For example, the time to reach the maximum conversion was 7 h at 60 °C but only 1.5 h at 120 °C. Notably, the highest yield of 4-aminostyrene with selectivity >90% was achieved at the time of just reaching a complete conversion of NS for the reaction conducted at 120 °C. A further reaction at prolonged time would lead to overhydrogenation to 4-ethylaniline.

Plot of ln*k* against the inverse of reaction temperature with the rate constants determined from the time evolution of NS concentration for each run is presented in Fig. 5b, which gave a straight line as $\ln k = -3.377(1000/T) + 12.91$ with a R^2 of 0.99.

According to the Arrhenius equation,

 $\ln k = \ln A - \mathrm{E}_{\mathrm{a}}/RT$

the apparent activation energy (E_a) and pre-exponential factor (A) were determined from the slope and intercept of the straight line for the four temperatures covered, which was ca. 28.1±2.0 kJ/mol, and 4.04±1.90×10⁵ mmol⁻¹ h⁻¹ g⁻¹Co MPa⁻¹, respectively. The activation energy measured in this work is similar to (or even slightly lower than) the values reported on precious metal-based catalysts (e.g., 30.8 kJ/mol for the nitrobenzene hydrogenation with Au/TiO₂ catalyst [26], 33 kJ/mol for the nitrobenzene hydrogenation with Ru/Iron oxide catalyst[81], and 31.2 kJ/mol for the reduction of 4-nitrophenol with Au NPs[82]). The low activation energy is probably related to the unique structrue of the Co/C-N materials.

3.5. Selective hydrogenation of nitroarenes

Under the optimized reaction conditions, the general scope of the novel Co/C-N-600 system was extensively investigated for the hydrogenation of various functionalized nitro compounds. From a synthetic point of view, it is useful but challenging that reducible moieties remained unaffected. Interestingly, halogen substituted nitrobenzenes were reduced to halogenatedanilines, which are known as key agrochemical intermediates, in excellent yields without any dehalogenation (Table 2, entries 1-4). Notably, even labile bromide- and iodo-nitroarenes were selectively hydrogenated in 99% yields, which are rarely reported in the hydrogenation catalysed by noble metals.

Moreover, sensitive functional groups such as aldehydes, ketones, nitriles, esters, amides, olefins, and even alkynes were also well tolerated in our catalytic system (Table 2, entries 5-18). In the presence of olefinic bonds, the yields of the desired anilines were obtained in 97-99% yields (Table 2, entries 5-7), which are comparable to the results reported in the literature [33,47,50].

Selective hydrogenation of the substrates bearing alkynes is most challenging and thus is rarely achieved [28,46,47,50]. In this respect, we are delighted to find our catalyst was also capable of reducing nitro groups in the presence of alkynes with full conversion and excellent selectivity (Table 2, entry 8). It is noteworthy that the

amino-benzonitriles, which constitute common building blocks for the chemical industry, could be obtained in up to 99% yield (Table 2, entry 9). An excellent yield was also gained although a prolonged reaction time was needed for the conversion of di-nitrile substituted nitroarenes (Table 2, entry 10).

The position of aldehydic substituent did not affect the reactivity significantly (Table 2, entries 11-12). Moreover, only the ortho- nitro group was reduced when nitro groups were present on benzaldehyde at both ortho- and para- positions (Table 2, entry 13). Interestingly, even prolonging the reaction time did not result in the reduction of the para- nitro group either. Furthermore, substrates that contained sensitive keto, amide, carboxylic acid, or ester substituents were also hydrogenated smoothly and selectively into the corresponding anilines in almost quantitative yields (Table 2, entries 14-18).

The amino-substituted N-heterocycles are important intermediates in pharmaceutical and agrochemical industries. Finally, we tested the hydrogenation of a variety of heterocyclic nitro compounds (Table 3). Again, all corresponding heteroaromatic amines were achieved in 95-99% yields. The above results suggest that the Co/C-N-600 material would be a promising catalyst for the clean and efficient production of functionalized arylamines via a chemoselective reduction of their corresponding nitroarenes with other reducible functional groups remaining intact.

4. Conclusions

In summary, we have develped a stable, inexpensive, and reusable Co/C-N catalyst for chemoselective hydrogenation of substituted nitroarenes to anilines with other reducible functional groups remaining intact. The novel cobalt-based catalyst is prepared by simple pyrolysis of ZIF-67, a typical MOF material, under inert atmosphere. It allows for highly selective hydrogenation of numerous structurally diverse nitroarenes in excellent yields under industrially viable conditions. In situ ATR-IR and XPS characterizations reveal that Co-N centers may be responsible for

the preferred adsorption and selective hydrogenation of nitro group as compared to other functional groups in nitroarenes. The kinetic study indicates a zero-order dependence on 4-nitrostyrene while a first-order dependence on H₂ pressure. Due to their facile operation on synthesis, separation, and reutilization, the stable and cost-effective materials would hold the potential for broad applications in green and economical synthesis of fine chemicals.

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Appendix A. Supplementary data.

Catalyst characterization, reaction results, and spectra data for the products. This material is available free of charge via the Internet at http://.

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Fig. 1. TEM images of Co/C-N-600 before (a) and after 5 runs of catalytic reaction (b).



Fig. 2. (a) Recycling of the Co/C-N-600 catalyst, conversion-black, selectivity-blue; (b) Leaching test with catalyst (blue) and with filtrate (black).



Fig. 3. In situ ATR-IR spectra of 4-nitrostyrene in Ar-saturated methanol solutions for

Co/C-N-600 at 25 °C (a), 100 °C (c); and Co/C-600 at 25 °C (b), 100 °C (d).



Fig. 4. XPS spectra of the N 1s region (a) for Co/C-N-600, and the Co 2p region (b) for Co/C-600 and Co/C-N-600.



Fig. 5. NS concentration as a function of time for four different temperatures (a) and the Arrhenius plot (b). Reaction conditions: NS (0.5 mmol), 1 MPa H₂.

Table 1

Hydrogenation of 4-nitrostyrene using different Co catalysts.^a

$H_2 (1MPa), 100 °C$							
Entry	Catalyst	Conversion (%)	Selectivity (%)				
1	ZIF-67	_	-				
2	Co/C-N-600	>99	97				
3	Co/C-N-700	83	75				
4	Co/C-N-800	80	63				
5	Co/C-N-900	75	52				
6 ^{<i>b</i>}	Co/C-N-600	>99	96				
7	Co/C-N-600-C	-	-				
8	Co/C-N-600-Co	4	98				
9 ^c	Co/C	-	-				
10^d	Co/C-600	30	50				
11	Pt/C	>99	0				
12	Pd/C	>99	0				
13	Ru/C	>99	0				
14	Rh/C	>99	0				
15 ^c	Ni/C	_	-				

^a Reaction conditions: 4-nitrostyrene (0.5 mmol), methanol (2 mL), catalyst (Co 15 mol%), 1 MPa

H₂, 100 °C, 3 h, *n*-hexadecane as an internal standard.

^b Catalyst (Co 1 mol%), 10 h.

^{*c*} Prepared by a colloidal deposition method.

^d Prepared by pyrolysis of Co-MOF-71 at 600 °C.

	IO ₂ Co/C-N-600	NH ₂		
ĸŢ	H ₂ (1MPa), 100 °C			
Entry	Substrate	Product	Time (h)	Yield (%) ^b
1	F NO ₂	F NH2	3	99
2			3	99
3	Br NO ₂	Br NH ₂	3	99
4 ^c		NH ₂	3	99
5	NO ₂	NH ₂	3	97
6		O NH ₂	7	99
7	NO ₂	NH ₂	4	99
8	NO ₂	NH ₂	3	93
9	N NO ₂	N NH2	3	99
10	N ^{MO} 2	N NH2	24	95
11	0, NO ₂	O NH2	4	98
12			4	99

Table 2 Selective hydrogenation of substituted nitroarenes.^a



^aReaction conditions: nitroarene (0.5 mmol), methanol (2 mL), Co/C-N-600 catalyst (Co 15 mol%), 1 MPa H₂, 100 °C. Conversions >99% were observed in all cases. ^bGC yield using *n*-hexadecane as an internal standard.

^cConducted in 1:1 THF-H₂O (2 mL).

Table 3

Entry	Substrate	Product	Time (h)	Yield (%) ^b
1 ^c			16	98
2	$\bigvee_{\substack{N \\ H}}^{N} \bigvee_{\substack{I \\ H}}^{NO_2}$		8	99
3		0 0 NH ₂	6	99
4		NH ₂	5	99
5			6	95
6	NO ₂	NH ₂	3	98

Selective hydrogenation of various nitroheterocycles.^a

^aReaction conditions: nitroheterocycle (0.5 mmol), methanol (2 mL), Co/C-N-600 catalyst (Co 15

mol%), 1 MPa H₂, 100 °C. Conversions >99% were observed in all cases.

^bGC yield using *n*-hexadecane as an internal standard.

^cConducted in 1:1 THF-H₂O (2 mL).