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Cobalt-modified molybdenum carbide as an efficient catalyst for chemoselective reduction of aromatic nitro compounds[†]

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This work presents a facile and clean transformation for synthesizing diverse functionalized arylamines through chemoselective reduction reaction of their corresponding substituted nitroarenes catalyzed by the supported cobalt-promoted molybdenum carbide catalyst on modified activated carbon (Co-Mo₂C/ AC, AC is denoted as the modified activated carbon by H₂O₂ oxidation treatment). Various characterization techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP) and H_2 temperature-programmed reduction (H_2 -TPR) were employed to reveal the relationship between catalyst nature and catalytic performance, and the plausible reaction mechanism is also proposed. The characterization results suggest that the addition of a small amount of transition metals, especially cobalt could significantly promote the formation of a perfect molybdenum carbide crystal phase, resulting in the improvement in catalytic properties of the supported molybdenum carbide catalyst. Reaction results demonstrate that the optimized Co-Mo₂C/AC catalyst shows comparable catalytic performance towards precious metals for chemoselective reduction of various aromatic nitro compounds, affording 100% yield for all substrates involved in this work (99.3% of isolated yield for model substrate). Moreover, it can be found that the catalyst could be easily recovered by filtration and recycled without obvious loss in its catalytic properties. Therefore, the developed Co-Mo₂C/AC catalyst in this work can be considered as an industrially viable and cheap candidate for clean and highly-efficient production of diverse functionalized arylamines.

Introduction

Functionalized arylamines, that serve as industrially important organic intermediates for producing pharmaceuticals, dyestuffs, functional polymers, *etc.*,¹ are mainly produced by chemoselective hydrogenation of the corresponding nitroarenes over metallic catalysts including noble metals such as Pt, Pd, Ru, Rh and non-noble metals such as Fe, Co, Ni, Cu and Zn catalysts.² In most cases, the precious metal catalysts were reported to be efficient for this transformation. In particular, the highly-efficient and magnetically recyclable Rh–Fe₃O₄ catalyst has been reported.^{2a} It is generally accepted that

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commercially available Ni or Pt catalysts cannot be used to hydrogenate substituted nitrobenzenes with H₂, since they lack the necessary chemoselectivity.^{2t} Because of this lack of selectivity and limited availability of the noble metals, Femediated catalysts have also been well developed, demonstrating high activity and selectivity for the synthesis of arylamines and realizing magnetic separation. However, adaptation for nitro-containing substrates and the reusability of the catalysts need to be improved. Moreover, sometimes harsh conditions are required for the reaction to proceed smoothly,^{2m-p} and therefore the catalytic activity needs to be further improved. Co is an alternative chemoselective catalyst for the production of functionalized arylamines.^{2r-t} However, KOH as an additive is required to promote the reaction on Co(II) substituted mesoporous aluminophosphate; although Co(n) phthalocyanine has high activity it was found to have poor reusability. The on-line prepared supported Co catalyst on carbon exhibited exciting catalytic activity, but the expensive ligands are indispensable. Au, Ag and Cu have been found to be selective for this reaction, but these catalysts were not active enough even under harsh reaction conditions.³ Therefore, it is highly desirable

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[†]Electronic supplementary information (ESI) available: The XRD, XPS, TPR, GC results for typical reaction mixture and GC for establishing degree of detectable sensitivity, GC results for reaction mixtures by using nitrosobenzene and phenyl-hydroxylamine as substrates, GC-MS, LC-MS and ¹H-NMR analytic results. See DOI: 10.1039/c3gc42049c

but challenging to develop a highly-efficient and less-expensive catalyst for chemoselective reduction of substituted nitroarenes to synthesize their corresponding arylamines.

In recent years, transition-metal carbides, such as Pt-like metals have attracted much attention as promising materials for their outstanding bulk and surface physicochemical properties.⁴ Previous reports reveal that metal carbides have been used as efficient catalysts and have been applied in decomposition reactions of hydrazine, ammonia and methanol, Fischer-Tropsch reaction, hydrogenolysis, water gas shift and electrocatalysis.⁵ Also they had been tried as additives or supports for precious metals to catalyze the reduction of nitroarenes. But the use of precious metals is indispensable.^{2a,6} The unique properties allow metal carbides to have great potential in hydrogen-transferring related reactions. The addition of transition metals has been found to enhance the formation of metal carbides.⁷ Thus, it can be envisioned that the metal carbide catalyst modified by appropriate less-expensive transition metals like Fe, Co, Ni, Cu or Cr may exhibit excellent catalytic performance for chemoselective reduction of nitroarenes. However, to the best of our knowledge, there have been no reports so far to utilize metal carbides as noble metal-free catalysts for the efficient transformation of substituted nitroarenes to corresponding functionalized arylamines.

In this study, we describe the first report of the facile and chemoselective reduction of nitroarenes containing other sensitive substituents to the corresponding functionalized arvlamines by using the supported cobalt-assisted molybdenum carbide on AC as an efficient precious metal-free catalyst (Scheme 1). The synergistic effect between cobalt and Mo₂C allows the catalyst to exhibit unexpected catalytic performance in this transformation. 100% conversion of various substrates with 100% selectivity of the corresponding functionalized arylamines has been achieved, which is comparable to the results for precious metal catalysts; in addition N₂ is the only byproduct, suggesting that this work presents a highly-efficient and clean approach for functionalized arylamines production. This work illustrates that metal carbides, once modified by an appropriate additive, can be considered as an efficient and low-cost alternative to precious metal catalysts for producing valuable functionalized arylamines. Moreover, this finding also opens a horizon to extend the application of this promising class of less-expensive metal carbides to replace scarce and highly expensive precious metals in the other organic reactions.



Scheme 1 Chemoselective reduction of various substituted nitroarenes to the corresponding functionalized arylamines over the developed supported metal carbide catalysts on AC.

Experimental section

General procedure for catalyst preparation

The as-received activated carbon derived from coconut shells (Aladdin Chemical Co., for catalyst support, China) was ground and sieved into a powder with grain size less than 62 µm for preparation of the catalyst support. The surface modification process of activated carbon via H₂O₂ oxidation was performed as follows. A given amount of ground activated carbon particles was immersed into 35 wt% H₂O₂ aqueous solution (10 ml g^{-1} AC) at 5–20 °C with continuous stirring for 6 h. The sample was filtered, washed with deionized water, and subsequently dried at 105 °C overnight, and then the AC supports were obtained. Afterwards, an aqueous solution containing M (M = Fe, Co, Ni, Cu or Cr) nitric acid compounds and ammonium molybdate with the desired M and Mo contents were impregnated onto the AC support using the incipient wetness impregnation (IWI) method as reported in the literature,8 followed by drying overnight and calcinating at a certain temperature in an N2 atmosphere to obtain MO_y -MoO_x/AC. Subsequently, a series of MO_v -MoO_x/AC were carburized in a CH₄-H₂ mixture as described previously,⁹ and finally passivated in 1% O2/N2 when the temperature was cooled down to room temperature. The resultant samples are the as-prepared M-Mo₂C/AC catalysts.

Characterization

XRD patterns were collected from 10 to 80° at a step width of 0.02° using Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a CuK α source (λ = 1.5406 Å). H₂-TPR experiments were performed in an in-house constructed system equipped with a TCD (thermal conductivity detector) to measure H₂ consumption. A quartz tube was loaded with 100 mg of catalyst pretreated by calcination in Ar at 300 °C for 30 min and then was cooled down to ambient temperature in Ar. After that, it was reduced with a 10 vol% H₂-Ar mixture (30 ml min⁻¹) by heating up to 800 °C at a ramp rate of 10 °C min⁻¹. XPS measurements were performed with a V.G. Scientific ESCALAB 250 spectrometer using monochromic Al K α ($h\nu$ = 1486.6 eV, 150 W). The binding energies of Mo 3d and Co 2p were analyzed at 220-240 and 775-805 eV, respectively, using the Shirley baseline-correction method. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as a reference. The leaching of the catalyst was investigated by measuring Co and Mo contents in reaction mixtures using the ICP technique on the ICP spectrometer (Optima 2000DV, Perkin Elmer).

Catalytic performance measurement

94 mg of catalyst prepared as in this work, 1 mmol nitrobenzene (Tianjin Beilian Fine Chemicals Corp., Ltd), the desired amount of hydrazine hydrate (80 wt%, Tianjin Bodi Chemicals Corp., Ltd), and ethanol (Tianjin Fuyu Chemicals Corp., Ltd) as solvent were added into a round-bottom flask, and the mixture was refluxed under strong stirring for the desired reaction time. In our experiments, all the reagents were analytical grade and used without further purification. The real hydrazine concentration calibrated in our lab is 79.2 wt%. Then the reaction mixture was cooled down to room temperature after the reaction finished. The catalyst was separated easily from the reaction mixture by a filtration procedure, and then it was washed with a certain amount of ethanol. The filtrate and washing liquid were combined to obtain the mixture for analysis. The mixture was quantitatively analyzed by gas chromatography (GC) and liquid chromatography (LC). The molecular structures of the obtained arylamines were confirmed by Mass Spectrometry (MS) and ¹H NMR (ESI[†]). The conversion was calculated by the weight percent of the consumed aromatic nitro compounds in the total amount added; the selectivity to arylamines was calculated by the weight percent of the desired product in the total products. The yields included in this paper are the GC or LC yield, except for the scaled-up experiment. The separated and washed catalyst was dried and reused for recyclability measurement without extra catalyst being added. In order to probe the perspective of the developed catalyst to practical application in industrial production, the experiment was scaled-up by a factor 10 and was performed on the basis of above procedure; the isolated yield was calculated as the percentage of the separated aniline through an evaporation method to the theoretical value based on the amount of nitrobenzene.

Results and discussion

The supported metal carbides (Mo₂C/AC and W₂C/AC) and the modified Mo₂C (M-Mo₂C/AC) catalysts on AC were prepared by the reported carbothermal reduction method.^{5a,b} From Fig. S1,[†] the shift of the XRD peaks towards Mo₂C phases from M-Mo₂C/AC catalysts shows the successful introduction of transition metals into the Mo₂C matrix. The nitrobenzene hydrogenation was used as a probe of the reaction to evaluate the catalytic performance of the obtained catalysts. The selectivity and yield were calculated based on GC analytical results. Table 1 illustrates the catalytic properties of various catalysts. As we all know, the possible reduction intermediates such as nitroso or phenylhydroxylamine in the reaction mixture may be highly carcinogenic, and therefore to establish a highly sensitive analysis method for investigating the possible existence of trace nitroso or phenylhydroxylamine is a very important issue. Firstly we investigated the degree of sensitivity of our analytical methods. We prepared an ethanol solution (due to ethanol being used as solvent in this work) with a total concentration of 10 ppm of possible reduction products including 4 ppm nitroso, 2.2 ppm phenylhydroxylamine and 3.8 ppm aniline as a sample. From the GC trace (Fig. S4b[†]), the three definitely detectable peaks at 4.38, 5.02 and 12.00 min corresponding to nitroso, aniline and phenylhydroxylamine, respectively, are observed, which shows that our analytical method possesses a sufficiently high degree of sensitivity for the detection of carcinogenic nitroso or phenylhydroxylamine as well as the desired product. From Fig. S4a,† only two GC peaks can be

Entry	Catalyst	Reaction time (h)	Sel./yield ^b (%)
1	25% W ₂ C/AC	1	100/29.9
2	25% Mo ₂ C/AC	1	100/40.6
3	2.5% Fe 25% Mo ₂ C/AC	1	100/73.9
4	2.5% Ni 25% Mo ₂ C/AC	1	100/82.4
5	2.5% Ni 25% Mo ₂ C/AC	2	100/92.0
6	2.5% Cu 25% Mo ₂ C/AC	1	100/77.7
7	2.5% Cr 25% Mo ₂ C/AC	1	100/73.9
8	2.5% Co 25% Mo ₂ C/AC	1	100/84.4
9	2.5% Co 25% Mo ₂ C/AC	2	100/100
10	Rh-Fe ₃ O ₄	1	$-/99^{c}$
11	2.5% Co/AC	1	100/21.4
12	AC	1	100/24.7
13	None	1	0
14	2.5% Co 25% Mo ₂ C/AC	2	$100/100^{d}$
15	2.5% Co 25% Mo ₂ C/AC	2	$100/100^{d}$
	—		

^{*a*} Reaction conditions: 94 mg catalyst, 1 mmol nitrobenzene, 2 equiv. N₂H₄·H₂O, calibration concentration of N₂H₄·H₂O is 79.2%. ^{*b*} Detected by GC-MS and ¹H-NMR. ^{*c*} From reference. ^{*d*} The nitrosobenzene and phenylhydroxylamine being used as substrates, respectively.

detected, corresponding to the solvent (ethanol) and aniline, and neither nitroso nor phenylhydroxylamine exists in the reaction mixture. Even if the GC is magnified to the same multiple as that in Fig. S4b,† there is still no peak corresponding to the nitroso or phenylhydroxylamine. Therefore, we can safely say that our analysis method is sensitive enough to exclude the existence of the carcinogenic nitroso and phenylhydroxylamine intermediates.

From Table 1, we can see that the as-prepared carbides, especially Mo₂C/AC modified with diverse transition metals, to be efficient catalysts for the chemoselective reduction of nitrobenzene with 100% of selectivity. No transformation in the blank experiment and poor reaction results over AC supports confirm the essential catalytic role of Mo₂C/AC in this transformation. However, the catalytic activity is depressed if the supported carbide is solely employed, which is consistent with the reported results.⁶ According to the previous reports, Fe, Co, Ni are active catalysts for the hydrogenation of nitrobenzene, although the selectivity is not satisfactory,^{7a-g} as well as demonstrating that Fe, Co and Ni promote the formation of molybdenum carbides,^{5a,7h} which suggest the possibility of a synergistic interaction between Fe, Co or Ni and Mo₂C. Therefore, we added some transition metals and investigated the promoting effect on the Mo₂C/AC catalyst. Interestingly, we found that the addition of a small amount of non-precious transition metals, especially cobalt can dramatically improve the conversion from 40.6% to 84.4% (100% selectivity), which is comparable with those over the reported noble-metal catalysts.^{2a} Through prolonging the reaction time up to 2 h, 100% conversion and 100% selectivity can be achieved, suggesting great potential in chemoselective reduction of functionalized nitroarenes. By using Ni as a promoting agent, only 92.0% yield can be obtained, although it has a comparable yield for 1 h to Co as promoting agent. As a result, Co is considered to be the superior promoting agent for this reduction reaction. The effect of loading of cobalt was optimized and the results

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are presented in Table S1 (ESI†). Results show that the amount of added cobalt has a visible effect on yield but no effect on selectivity, and the 2.5% of optimal loading of additive is essential for achieving high yield. To elucidate the promoting effect of the added cobalt on the catalytic performance of the supported Mo₂C catalyst on AC for the chemoselective reduction of nitroarenes, the two samples 25% Mo₂C/AC and 2.5% Co/AC were also tested. In a comparison of the 25% Mo₂C/AC and 2.5% Co/AC, the combined catalyst (2.5% Co– 25% Mo₂C/AC) exhibits unexpectedly better catalytic activity, implying the existence of the notable promoting effect of the addition of Co. Various techniques like XRD, XPS and H₂-TPR were employed to further probe the roles of adding Co in improving the catalytic performance.

Fig. 1(A) presents the XRD patterns of as-prepared Mo₂C/AC catalysts with and without Co modification. The diffraction peaks at 34.6°, 38.1°, 39.6°, 52.4°, 61.8°, 69.8°, 74.7° and 75.7° can be assigned to the (100), (002), (101), (102), (110), (103), (112) and (201) crystal faces of β -Mo₂C with a hexagonal close-packed structure (PDF# 35-0787)^{5c,10} (Fig. 1A). Furthermore, no



Fig. 1 (A) XRD patterns and (B) XPS spectra of 25% Mo_2C/AC and 2.5% Co 25% Mo_2C/AC catalysts.

visible peak corresponding to Co can be detected, which is ascribed to the fine dispersion of Co or the insertion into the β-Mo₂C matrix (the cobalt is definitely introduced into the sample, confirmed by Co 2p XPS data in Fig. S2, ESI⁺). Through carefully comparing the XRD patterns of Co-modified and unmodified Mo₂C/AC catalysts, a slight shift to higher diffraction angle in comparison with unmodified sample can be observed, implying the incorporation of Co into the β -Mo₂C crystal phase. Thus it allows the existence of a strong interaction between Co and Mo₂C. The remarkable high intensity of the diffraction peaks in Co-Mo₂C/AC in comparison with those obtained from Mo₂C/AC (collected under the same conditions) implies the promoting effect of Co on the formation of crystal Mo₂C, consistent with the previous reports.^{5a,7h} The broadened XRD peaks show that the unmodified Mo₂C/AC catalyst has smaller average crystalline size than Co-Mo₂C/AC. Generally, the smaller size is favorable for enhancing reaction. However, the Co-modified Mo₂C catalyst with larger average crystalline size exhibits the significantly superior catalytic performance to the unmodified Mo₂C catalyst, which shows the excellent catalytic performance of Co-Mo₂C/AC catalyst is a result of the possible synergistic effect between Co and Mo₂C, but not from the average crystalline size. The Mo 3d XPS spectra of the Co-modified and unmodified Mo₂C/AC catalysts are given in Fig. 1(B). The peaks at 229.5 and 232.6 eV assigned to Mo⁴⁺ and Mo⁶⁺ in the carbides^{5b,7h,11} become weaker and shift to lower binding energy as the cobalt is introduced, further suggesting the existence of the interaction between cobalt and Mo₂C,^{5*a*,7*h*} which is consistent with those reported in references. 5a,b,7h,11 From the H₂-TPR profiles, 12 the second peak corresponding to MoO3 from Co-modified MoO3/AC shows a remarkable shift to lower temperature in comparison with that obtained from the unmodified one (Fig. S3 in ESI⁺), suggesting the promoting effect of Co on the reducibility of MoO₃, which may be favorable for the formation of carbide via a carbothermal reduction method.^{5a,7h} The confirmed synergistic interaction between Co and Mo₂C significantly improves the catalytic performance of Mo₂C in chemoselective reduction of nitro groups.

A plausible reaction mechanism is proposed (Scheme 2). The tungsten and molybdenum carbides are highly active catalysts for the decomposition of $N_2H_4^{-7j,k}$ and active H and N



Scheme 2 Plausible reaction mechanism for the reduction of nitroarenes over $Co-Mo_2C/AC$ in the presence of hydrazine hydrate.



Fig. 2 Recyclability test of the developed 2.5% Co 25% Mo₂C/AC catalyst for chemoselective reduction of nitrobenzene to yield aniline. Conditions: 94 mg catalyst, 1 mmol nitrobenzene, 2 equiv. N_2H_4 · H_2O , at refluxing temperature for 2 h of reaction time.

atoms can be formed. The addition of transition metals has been found to enhance the formation of metal carbides, which can efficiently catalyze many reactions by the synergistic effect between the metal carbide and transition metals like Fe, Co and Ni.7 The synergism can hopefully enhance the activation of N₂H₄. As a result, the chemoselective reduction of nitroarenes can take place smoothly over the developed Co-promoted Mo₂C/AC catalyst. The active N atoms can be transformed into N₂ which is harmless for the environment while the active H atoms (some of the active H is transformed into H₂, and therefore excess N₂H₄ is required) as the source of the reducing agent leads to the quick reduction of the nitro group to produce a nitroso intermediate, with subsequent fast conversion to phenylhydroxylamine, followed by final reduction in the rate-determining step to the product aniline; a similar mechanistic profile has been also proposed in the literature.^{7i,13} In order to confirm that the effective reducing agent is the active H atom and not the formed H₂ (H₂ can be produced by decomposition of N₂H₄^{7j}), we performed the Co-Mo₂C/AC catalyzed reduction of nitrobenzene at 5 bar of hydrogen pressure, but no detectable aniline is formed. According to the reported reference,^{2m} only a 1% trace of aniline was detected in the presence of N₂H₄ (without adding catalyst), implying that N₂H₄ is not the reducing species. From above, neither H₂ nor N₂H₄ is an effective reducing species but it is the active H atom formed on-line by the decomposition of N₂H₄. The proposed reaction mechanism is further confirmed. From references,¹³ the nitrosobenzene and phenylhydroxylamine are the possible intermediates in the reduction process of nitroarenes by using N₂H₄ as reducing agent. In order to shed further light on the above mechanism, the control experiments using nitrosobenzene and phenylhydroxylamine intermediates as substrates in the same reaction conditions as those for chemoselective reduction of nitrobenzene were performed, and the reaction results are listed in Table 1 (entries 14 and 15). The reaction results demonstrate that the aniline is

Entry	Substrate	Product	N ₂ H ₄ ·H ₂ O (equiv.)	Reaction time (h)	Sel./yield ^t (%)
1	NO ₂	NH ₂	2	2	100/100
2		NH ₂	2	2	100/100 ^c
3	NO ₂	NH ₂	2	2	100/99.3 ^d
4	NO ₂ Cl	NH ₂ Cl	6	1	100/100
5		NH ₂	6	1	100/100
6			6	1	100/100
7	NO ₂ OH	NH ₂ OH	6	1	100/100
8		NH ₂	7	3	100/100
9	OH NO ₂	OH NH ₂	1	1	100/100
10			6	1	100/100 ^e
11		NH ₂	6	1	100/100
12	NO ₂	NH2	6	1	100/100
13	OCH3	OCH3	10	3	100/100

Entry	Substrate	Product	$\begin{array}{l} N_2H_4{\cdot}H_2O\\ (equiv.) \end{array}$	Reaction time (h)	Sel./yield ^b (%)
14	NO ₂	NH2 NH2 NH2	8	2	100/100
15	NH2 NO2	NH2 NH2 NH2	14	3	100/100
16	NH ₂ Cl	NH ₂ Cl	6	1	100/100
17	NO ₂ CH ₃	CH3	6	1	100/100
18	NO ₂	NH ₂	6	1	100/100

 a Reaction conditions: 94 mg catalyst, 1 mmol substrate, 80% of N₂H₄ aqueous solution as reducing reagent. b Detected by GC-MS and ¹H-NMR. c Scaled up by factor 10. d Isolated yield. e LC-MS was used (in ESI).

the only product (Fig. S5–S7†) for the nitrosobenzene, phenylhydroxylamine or nitrobenzene as substrate of chemoselective reduction. Correlated to the former mechanism analysis and reference, the control experimental results further confirm the above proposed reaction route for the chemoselective reduction of nitro group over the developed Co-promoted Mo_2C/AC catalyst in this work.

In industrialized production, the catalyst recycling is definitely important in the heterogeneous catalytic reactions. Therefore, we investigated the recyclability of our developed catalyst for chemoselective reduction reaction by using nitrobenzene as a model substrate. The separated spent catalyst was used only by washing with ethanol and drying before use, with no extra fresh catalyst being added. Fig. 2 presents the experimental results. From the reaction results, we can observe that there is no loss in the yields of aromatic anilines over eight recycling runs of the used catalyst, suggesting the potential catalyst for the chemoselective reduction of nitroarenes in practical applications.

As we know, the scaled-up catalytic properties and isolated yield are very important for a practical catalyst, and thereby using nitrobenzene as a model substrate, the experiment scaled-up by a factor 10 was performed, and the GC yield and isolated yield are presented in Table 2 (entries 2 and 3). Reaction results show that no difference in selectivity and GC yield take place if the reaction is scaled-up by factor 10, as well as 99.3% of isolated yield can be obtained, which is very close to the GC yield. From above, the non-precious metal Co-Mo₂C/AC catalysed chemoselective reduction could be a practical approach for the production of arylamines. Leaching of catalyst can lead to the residual metal in the chemical product, besides the deactivation of catalyst. Therefore, the investigation on leaching of the catalyst is quite important for a practical catalyst. We carefully performed the leaching experiments through ICP analysis, finding that only 0.1544 and 2.336 ppm of Co and Mo, respectively can be detected. Therefore, the leaching of Co and Mo is negligible.

To investigate the scope of the developed method in this work, the reduction reactions of structurally diverse nitro compounds were carried out, and reaction conditions were also optimized (Table S2, ESI†). The optimized reaction results are presented in Table 2.

From Table 2, the catalyst has excellent selectivity and yield for the chemoselective reduction of various functionalized nitroaromatics under the optimized reaction conditions (the details can be seen in Table S2, ESI[†]). Interestingly, halogen substituted nitrobenzenes were reduced to the corresponding chloroanilines in high yields and without any dehalogenation (Table 2, entries 4-6). The reducible functional groups in reaction substrates like OH, CHO, COOC₂H₅ and COOH remained totally unaffected under the reaction conditions (Table 2, entries 7-11). Notably, the reduction reactions of nitroaniline also occurred selectively to give the corresponding phenyl diamines with 100% selectivity (Table 2, entries 13 and 14). The multiamino aromatic compounds, as key fragments in dyes, can also be efficiently and selectively produced by the chemoselective reduction of corresponding nitroarenes using the developed Co-Mo₂C/AC catalysts (Table 2, entries 15 and 16). The above results exhibit the developed Co-Mo₂C/AC material in this work is a promising catalyst for the clean and efficient production of functionalized arylamines via a chemoselective reduction reaction from their corresponding nitroarenes, the vulnerable moieties in the various substrates were well tolerated during the reaction process in this approach.

In summary, we present an efficient and practical approach for the chemoselective synthesis of various functionalized arylamines from corresponding nitroarenes by Co modified metal carbides whose catalytic properties are comparable to those of precious metals, which is ascribed to the remarkably synergistic effect between Co and Mo₂C confirmed by XRD, XPS, H2-TPR and a test reaction as well. The catalyst can be easily separated and reused eight times without any loss in its catalytic performance. ICP analysis shows no obvious leaching of the catalyst, suggesting a very low concentration of residual transition metals in the product. In view of the importance of functionalized arylamines in industrial manufacture, the strategy presented in this work, once fully developed, may open a window for the production of valuable amine-containing chemicals from nitro groups. In addition, the substitution of precious metal catalysts with less-expensive transition metal carbides in various transformation reactions will be of great

importance due to the limited availability and high cost of noble metals.

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