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Synergistic effect from Lewis acid and the Ni-W_2C/AC catalyst for highly active and selective hydrogenation of aryl nitro to aryl amine†

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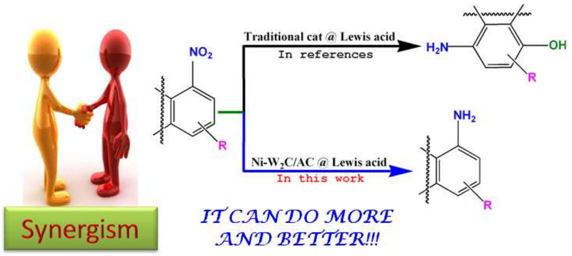
Graphic Abstract

Highly-active and selective hydrogenation of nitroarenes to their corresponding aromatic amines by synergism from Ni-W_2C/AC and Lewis acid is presented.



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PAPER

Synergistic effect from Lewis acid and the Ni-W_2C/AC catalyst for highly active and selective hydrogenation of aryl nitro to aryl amine†

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This work presents a facile approach for clean and chemoselective syntheis of various functionalized arylamines from their corresponding substituted nitroarenes through the unexpected synergistic effect of Lewis acid and Ni-W_2C/AC catalyst, affording almost 100% of arylamine yield. The results challenge the long-held axiom that the combination of Lewis acid and hydrogenation catalyst mainly enhances the transformation of nitrobenzene (NB) to p-aminophenol via Bamberger rearrangement of the formed intermediate phenylhydroxyamine (PHA) under catalytic hydrogenation conditions. X-ray diffraction (XRD) and FT-IR spectroscopy were employed to reveal the relationship between catalyst nature and catalytic performance, and the plausible reaction mechanism is also proposed. Reaction results demonstrate that the $FeCl_3$-Ni-W_2C/AC catalytic system 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 (99.5% of isolated yield for model substrate). Moreover, it can be found that the catalyst could be easily recovered by filtration and recycled without visible loss in its catalytic activity. Therefore, the developed $FeCl_3$-Ni-W_2C/AC catalytic system in this work can be considered as a practical candidate for clean and highly-efficient synthesis of diverse functionalized arylamines. We believe this approach can be extended to the other hydrogenation reactions.

Introduction

Functionalized arylamines serve as industrially important organic intermediates for producing pharmaceuticals, dyestuffs, functional polymers and rubbers.[1-3] The chemoselective hydrogenation of diverse nitroarenes has considered as an efficient and clean strategy to synthesize the corresponding functionalized arylamines, is one of the most active topics in applied and fundamental catalytic research. For its importance, a number of methods, including stoichiometric reducing agents,[4-6] metal-catalyzed hydrogenation featuring various reducing agents to reduce nitroarenes have been developed.[7-11] Among them, catalytic hydrogenation is of particular interest owing to its environmental friendliness, atomic efficiency, and compatibility with industrial processes.[12-14] The sustainable development demands highly active and selective catalysts for the hydrogenation of substituted nitroarenes. Unfortunately, the existing catalysts have often failed to meet the dual requirements of activity and selectivity. On one hand, the most common commercially available Raney nickel and palladium catalysts are widely employed,[15-18] though they show high activities for nitrobenzene hydrogenation, the selectivity to the hydrogenation of many functionalized nitroarenes, especially chloronitrobenzene, still remains low because of co-existing dehalogenation reaction. On the other hand, platinum, rhodium and ruthenium based atalysts have also been deeply investigated,[19-28] although they have shown interesting catalytic performance under mild reaction conditions, they are not suitable for an industrial expansion due to their high cost and limited availability. Based on the above issues, there are emerging numerous non-noble metal catalysts such as Fe, Co, Ni, Cu and Zn based catalysts,[29-41] whereas, the high hydrogenation ability of Ni based catalysts usually proceeds the hydrogenation of other groups existing in the arene substrates, leading to undesirable byproducts or the use of Ni–B, Ni-P, NiPB and NiCoB metallic systems have been examined as possible means of enhancing their selectivity.[42-49] However, the associated complexity and costs militate against the viability of these approaches in terms of process scale up. Besides Ni based catalysts, Cu based catalysts have also been found to be selective for this reaction, but these catalysts were not active enough even under harsh reaction conditions.[37] Co based catalysts are another choice, breakthrough progress has been made in recent days, nevertheless, expensive ligand and high pressure are essential for promoting the reaction to proceed smoothly, recycling problems still exist in this catalytic system.[50] Above all, we can conclude that precious metals exhibit excellent activity in the hydrogenation of nitroarenes compared with non-precious metals, however, considering the limits of their resources and high price, thus there is now a pressing need to develop an inexpensive and efficient non-noble metal catalysts repalcing the noble metals to promote the selective hydrogenation of aromatic nitroarenes.

Transition-metal carbides, as Pt-like metals have attracted much attention as promising material for their outstanding bulk

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† Electronic Supplementary Information (ESI) available: Degree of GC sensitivity, XRD, H_2-TPR, GC-MS, LC-MS and ^{1}H-NMR analytic results. See DOI: 10.1039/c3ra000000x/

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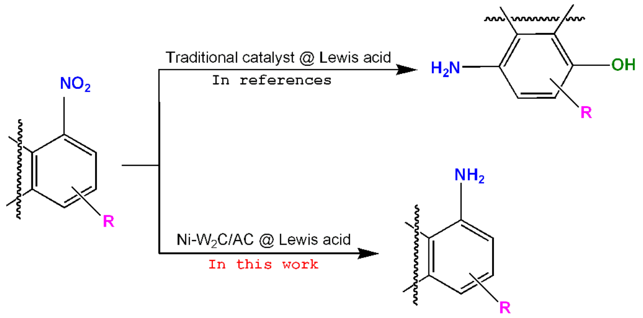
and surface physicochemical properties,[51,52] therefore it's eager to employ transition metal carbide catalyst in the hydrogenation of nitroarenes with excellent activity and high selectivity. According to the reported literature that transition metal carbide had been attempted as additives or supports for precious metal catalyzed hydrogenation of nitroarenes using hydrazine hydrate as a hydrogen source, but the usage of precious metals is indispensable.[53,54] Many reports have demonstrated that the supported metal carbide exhibits higher catalytic performance compared with the unsupported carbide catalysts, ascribed to high surface area, high sintering-tolerrance stability, and the possible metal-support interaction.[55-59] In our precious work, we have employed supported transition metal molybdenum carbide catalysts in the hydrogenation of functionalized nitroarenes using hydrazine hydrate as hydrogen source[60], therefore, transition metal carbide has great potential for the hydrogenation of nitroarenes under the condition of hydrogen. From the viewpoint of economic and clean production, to replace hydrazine hydrate by hydrogen is highly desirable. In this approach, the catalytic performance of metal carbide catalysts for chemoselective hydrogenation of nitroarenes using hydrogen as reducing agent has been investigated.

It has been reported that the existing synergistic effect between Lewis acid and various catalysts can notably enhance the diverse hydrogenation reactions.[61-69] However, in the presence of Lewis acid, due to the Bamberger rearrangement of the formed intermediate phenylhydroxyamine (PHA) in process of catalytic hydrogenation of nitrobenzene, the produced chemical is *p*-aminophenol but not aniline,[70-72] From the reference, the existence of CO_2 may enhance the catalytic performance of Ni for the hydrogenation of nitrobenzene to aniline due to the dual roles of Lewis acid and base of CO_2.[69] Due to the weak basic properties of metal carbide,[73,74] we speculate that the addition of Lewis acid into the reaction systems to cooperate with transition metal carbides may exhibit high catalytic performance for the hydrogenation of nitroarenes.

In this work, we present the first approach of the efficient and chemoselective hydrogenation of nitrobenzene to aniline over the Ni-W_2C/AC catalyst on the basis of unexpected synergistic effect (100% conversion and 100% selectivity). In this approach, no rearrangement but only highly selective hydrogenation products can be detected over Ni-W_2C/AC catalyst in the presence of Lewis acid, as well as obvious enhancing effect of adding Lewis acid can be observed due to the unexpected synergism between Lewis acid and Ni-W_2C/AC, which challenges the long-held axiom that the combination of Lewis acid and hydrogenation catalyst mainly enhances the transformation of nitrobenzene (NB) to aminophenol under hydrogenation conditions (Scheme 1). The developed strategy of Lewis acid-metal carbide synergistically catalyzed hydrogenation of nitro group can be extended to various nitroarenes, can be considered as an efficient and low-cost alternative to precious metal catalysts for functionalized arylamine production. The developed precious metal-free catalytic system can be recycled eight times without visible loss in catalytic performance and it is also extended to vaious substrates, suggesting its industrial interest. This finding can pave a new avenue for the use of synergism between catalyst and Lewis acid in the other organic transformations.



Scheme 1 A comparison of the Ni-W2C/AC@Lewis acid in this work and traditional catalyst @Lewis acid for catalytic hydrogenation of nitroaromatics.[61-69]

Experimental Section

General procedure for catalyst preparation

The as-received activated carbn derived from coconut shells (Aladdin, special for catalyst support, China) was ground and sieved into powders with grain size less than 62 μm for preparing catalyst support. The surface modification process of activated carbon via H_2O_2 oxidation was performed as following: a given amount of ground activated carbon was immersed into a 35 wt% H_2O_2 aqueous solution (10 ml g^{-1}AC) at 5-20 °C with continuously 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 of M (M = Fe, Co, Ni and Cu) nitric acid compounds and ammonium tungstate solution containing desired M and W contents were impregnated onto the AC support using incipient wetness impregnation (IWI) method as reported in literatures,[75,76] followed by drying overnight and calcinating at a certain temperature in N_2 atmosphere to obtain MOy-WOx/AC, subsequently, the series of MOy-WOx/AC were carburized in CH_4/H_2 mixture based on references,[77-80] finally passivated in 1% O_2/N_2 when the temperature cooled to room temperature, The resultant sample are denoted as M-W_2C/AC cataysts.

Characterization

X-ray diffraction (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 CuKα source (λ=1.5406 Å). H_2 temperature-programmed reduction (H_2-TPR) experiments were performed in an in-house constructed system equipped with a TCD (thermal conductivity detector) to measure H_2 consumption. A quartz tube was loaded with 100 mg of catalyst which was pretreated by calcination in Ar at 300 °C for 30 min and then was cooled to ambient temperature in Ar. After that, it was reduced with a 10 vol.% H_2/Ar mixture (30 ml min^{-1}) by heating up to 800 °C at a ramp rate of 10 °C min^{-1}. The FTIR was used to examine the interactions of reacting species with catalytic system. The FTIR spectra of NB, nitrosobenzene (NSB), and PHA with catalytic systems like single Lewis acid, Ni-W_2C/AC and the combined Lewis acid and Ni-W_2C/AC system (after sufferring from reaction temperature and pressure but not adding H_2) were collected with the same spectrometer, as well as the FTIR spectra of pure liquids containing NB, NSB or PHA,

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respectively were also collected for comprison.

Catalytic performance measurement

Catalytic measurements were performed in a 50 mL stainless steel autoclave batch reactor. In a typical experiment, 50 mg of the as-prepared catalyst, 15 g of the solvent (cyclohexane, Tianjin Fuyu Chemials Corp., Ltd) and 4.1 mmol of nitrobenzene (Tianjin Beilian Fine Chemcials Corp., Ltd), and the desired amount of Lewis acids were put into the reactor and purged 3 times with N_2 to replace the air in the reactor and purged 3 times with H_2 to replace the N_2 for 3 times at room temperature respectively. In our experiments, all the reagents were analytical grade and used without further purification. The reaction was then carried out at 240 °C and a H_2 pressure of 2.5 MPa for 2.5 h under vigorous stirring (1000 rpm), the pressure in the reactor gradually dropped, indicating the conversion of nitrobenzene. After appropriate reaction time, the temperature was lowered quickly in an ice-water bath and the hydrogen pressure was released, then the catalysts were separated from the products by easily filtration, washed thoroughly with cyclohexane three times, and then reused in the next catalytic cycle under the same conditions. 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 series of arylamines were confirmed by Mass Spectrometer (MS) and 1H NMR (Fig. S5 and S6, in ESI†). The conversion was calculated by weight percent of the consumed aromatic nitro compounds in the added total amount; the selectivity to arylamines was calculated by 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 seperated and washed catalyst was dried and reused for recyclability measurement without extra catalyst being added. In order to probe the perspective of practical application in industrial production towards the developed catalyst, the scaled-up experiment by factor 10 was performed on the basis of above procedure, and the isolated yield was calculated by the percentage of the seperated aniline through evaporation method to the theoretical value based on the amount of nitrobenzene.

Results and discussion

Characterization of the catalyst

We prepared the supported metal carbides (Mo_2C and W_2C) and the modified W_2C (M-W_2C/AC, M= Fe, Co, Ni and Cu) catalysts on AC according to the reported carbothermal reduction method.[81,82] XRD and H2-TPR experiments were performed to further probe the roles of adding transition metals in improving the catalytic performance. Fig. 1(A) presents the XRD patterns of as-prepared W2C/AC catalysts with and without transition metal modification. The diffraction peaks at 34.32, 37.79, and 39.40° were detected, assigned to W_2C phases with hexagonal closed packed structure (PDF#20-1315), and the diffraction peaks existing at 48.16° can be assigned to WC phase (PDF#65-8828). The visible peaks towards Ni, Fe, Co, Cu on the modified, associated with the no obvious shift for the peaks assigned to W_2C or WC, implying no obvious insertion of transition metal into metal carbide matrix. The supported W_2C catalyst on AC can be prepared via carbothermal reduction method,[81] we performed the H_2-TPR experiments on the oxide state precursors of the diverse transition metals modified supported W_2C catalysts to investigate the effect of the addition of transition metals on the redox of supported WO_3 by using the same amount of samples. The profiles are presented in Fig. 2(B). There are two or three peaks on the profiles of the modified catalysts. The peaks at low temperature can be assigned to the reduction of high valent W species to low valent ones, and the reduction of trandition metal oxides to metals; as well as the last peak can be indexed as the reduction of low valent W oxide to zero valent metal. The latter is crucial for the formation of metal carbide. From Fig. 1B, the last peaks corresponding to the reduction of lower WO_x to metal W shows a shift to lower temperature in some degree while the diverse transition metals except for Cu were added, suggesting the addition of Fe, Co or Ni enhances the reduction of WOx, possibly arising from the transition metals promoted H_2 dissociation to assist the reduction of WO_x.[81] As a result, the formation of W_2C and WC phases was enhanced, consistent with the previous reports.[81,83] This promoting process can be further proved by the XRD in Fig. 1A, and the more sharp and strong

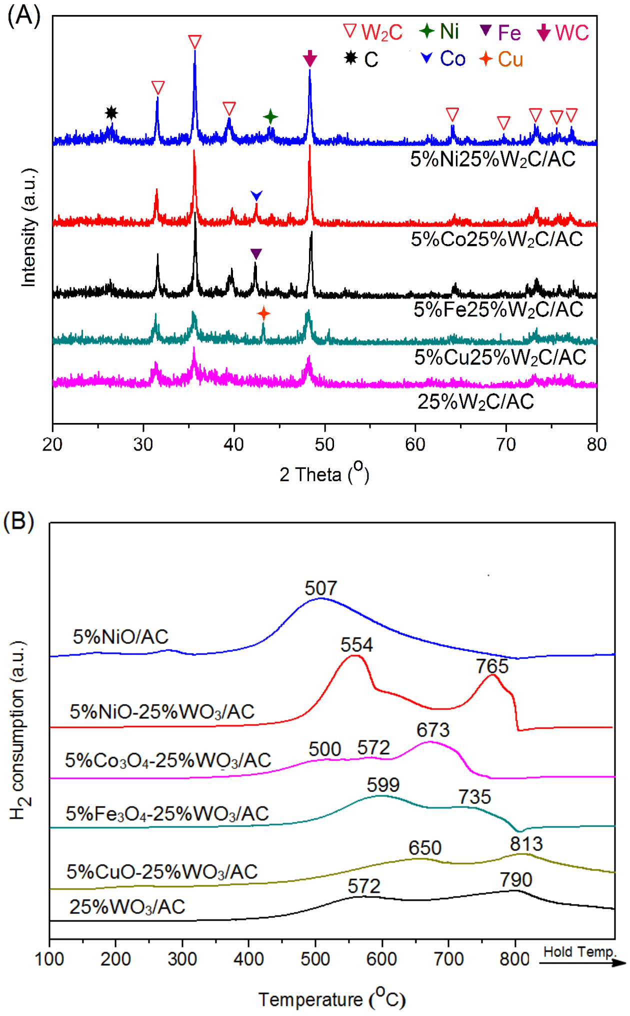

Fig.1 (A) XRD patterns and (B) H_2-TPR patterns of modified and unmodified W_2C/AC catalysts.

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peaks towards carbide on the modified W_2C/AC than on the unmodified one can be observed, suggesting that the addition of tansition metals doesn't change the dispersity of W_2C on the support. The promotion effect of adding transition metals on the formation of carbide mainly resulted from the enhanced H_2 dissociation on transition metals.[84] This kind of promoting effect can efficiently improve the catalytic performance of supported W_2C catalyst on AC for chemoselective hydrogenation of nitro groups. Moreover, although the reduction peak corresponding to NiO on the NiO-WO_3/AC sample shifts to higher temperature in comparison of that on 5%NiO/AC, the added Ni also can promote the hydrogenation of nitro compounds, since the Ni is active for the H_2 adissociation. That is to say, the addition of transition metals, especially Ni can synergistically promote the W_2C/AC catalyzed hydrogenation reaction through the two possible aspects: one is to promote the formation metal carbide, the other is its inherent catalysis on this reaction.

Optimization of reaction

The nitrobenzene was used as a probe molecule to evaluate the catalytic performance of the obtained catalysts for hydrogenation of nitroarenes. The selectivity and yield were calculated based on GC analytical results. Table 1 illustrates the catalytic properties of various catalysts without the addition of Lewis acid. As we all know, the possible existing hydrogenation intermediates like nitrosobenzene (NSB) or PHA in reaction mixture may be highly carcinogenic, and therefore to establish high sensitive analysis method and to investigate the possible existence of trace nitroso or phenylhydroxylamine are very important issues. In our previous report,[60] it has been established that our analysis method is sensitive enough to exclude the existence of the carcinogenic nitroso and phenylhydroxylamine intermediates. From Table 1, it can be observed that the supported metal carbide catalysts on AC, especially Ni modified W_2C/AC to be promising catalysts for the chemoselective hydrogenation of nitrobenzene with 100% of selectivity. Only 4.9% of yield in the blank experiment or over bare AC support confirm the essential catalytic role of W_2C/AC in this transformation. 25% of optimal W_2C loading is required for achieving high yield. However, the catalytic activity is depressed if the supported carbide is solely employed, which is consistent with the reported results.[60] According to the previous reports, Fe, Co, Ni are active catalysts for the hydrogenation of nitrobenzene, although the selectivity is not satisfactory,[7,37,42] as well as the Fe, Co and Ni are demonstrated to promote the formation of molybdenum carbides,[82,83] which suggest the possibility of synergistic interaction between Fe, Co or Ni and Mo_2C. Therefore, we added some transition metals and investigated the promoting effect on the Mo_2C/AC catalyst. Interestingly, we illustarte that the addition of a small amount of non-precious transition metals, especially Ni can dramatically improve the conversion from 35% to 52% (100% selectivity). The Ni loadings were optimized to improve the catalytic performance by diversing the loading from 3 to 7% (Entries 10, 12, 13, 14, 15, Table 1), and 5% of optimum Ni loading is indispensable to achieve 52% of higher yiled. In order to elucidate the promoting effect of the added Ni on the catalytic performance of the supported W_2C catalyst on AC for the chemoselective hydrogenation of nitroarenes, the two samples 25% W_2C/AC and 5% Ni/AC were also tested. In comparison of the 25% W_2C/AC or 5% Ni/AC, the incorporated catalyst (5% Co-25% W_2C/AC) exhibits unexpectedly better catalytic activity, even much better than the physically mixed 25% W_2C/AC or 5% Ni/AC, implying the existence of synergistic effect between Ni and W_2C for chemoselective hydrogenation.

Table 1 Hydrogenation of nitrobenzene over various catalysts[a]

Entry	Catalyst	Sel./Yield (%)[b]
1	None	100/4.9
2	AC	100/4.9
3	25%Mo_2C/AC	100/17.3
4	25%W_2C/AC	100/35.0
5	15%W_2C/AC	100/22.0
6	20%W_2C/AC	100/28.0
7	30%W_2C/AC	100/32.0
8	5%Fe25%W_2C/AC	100/43.7
9	5%Co25%W_2C/AC	100/45.0
10	5%Ni25%W_2C/AC	100/52.0
11	5%Cu25%W_2C/AC	100/39.7
12	3%Ni25%W_2C/AC	100/36.0
13	4%Ni25%W_2C/AC	100/48.4
14	6%Ni25%W_2C/AC	100/50.7
15	7%Ni25%W_2C/AC	100/47.0
16	5%Ni/AC	100/19.0
17	5%Ni/AC+25%W_2C/AC	100/42.0

[a] Reaction conditions: 50 mg catalyst, 4.1 mmol nitrobenzene, P_{H2}=2.5 MPa, T=240 °C, t=2.5 h; [b] detected by GC-MS and ^{1}H-NMR.

Through adding Ni into W_2C/AC catalyst, the catalytic performance of suppurted carbide catalyst has been notably improved. However, the only 52% of yield can be obtained. The improvement in catalytic activity of Ni-W_2C/AC for chemoselective hydrogenation is highly desirable. The synergistic effect between Lewis acid and hydrogenation catalyst on efficiently promoting the other hydrogenation process but not nitro group hydrogenation have been reported,[61-69] we proposed the addition of Lewis acid into the hydrogenation reaction systems over Ni-W_2C/AC catalyst may significantly promote the hydrogenation of nitroarenes. Once the improved chemoselective hydrogenation of nitro on the basis of synergistic effect between Lewis acid and Ni-W_2C/AC catalyst can be succeedfully established, the concept for Lewis acid promoting Bamberger rearrangement of the formed intermediate phenylhydroxyamine (PHA) in process of catalytic hydrogenation of nitrobenzene to produce *p*-aminophenol but not aniline,[70-72] would be broken.

Under the same conditions, the catalytic hydrogenation

Table 2 Hydrogenation of nitrobenzene over 5%Ni-25%W_2C/AC catalysts with and without the addition of different promoting additives.[a]

Entry	Catalyst	Additives	Sel./Yield (%)[b]
1	-	Anhydrous $FeCl_3$	100/9.2
2	5%Ni25%W_2C/AC	-	100/52.0
3	5%Ni25%W_2C/AC	Anhydrous $FeCl_3$	100/100
4	5%Ni25%W_2C/AC	Anhydrous $AlCl_3$	100/97.0
5	5%Ni25%W_2C/AC	Anhydrous $SnCl_2$	100/97.3
6	5%Ni25%W_2C/AC	Anhydrous $Fe(NO_3)_3$	100/64.0
7	5%Ni25%W_2C/AC	Anhydrous $FeCl_2$	100/74.0
8	5%Ni25%W_2C/AC	Anhydrous $FeCl_3$	100/100[c]
9	5%Ni25%W_2C/AC	Anhydrous $FeCl_3$	100/100[d]

[a] Reaction conditions: 50 mg catalyst, 0.02 g additives 4.1 mmol nitrobenzene, P_{H2}=2.5 MPa, T=240 °C, t=2.5 h; [b] detected by GC-MS and ^{1}H-NMR; [c,d] the nitrosobenzene and phenyldroxylamine being used as substrates, respectively.

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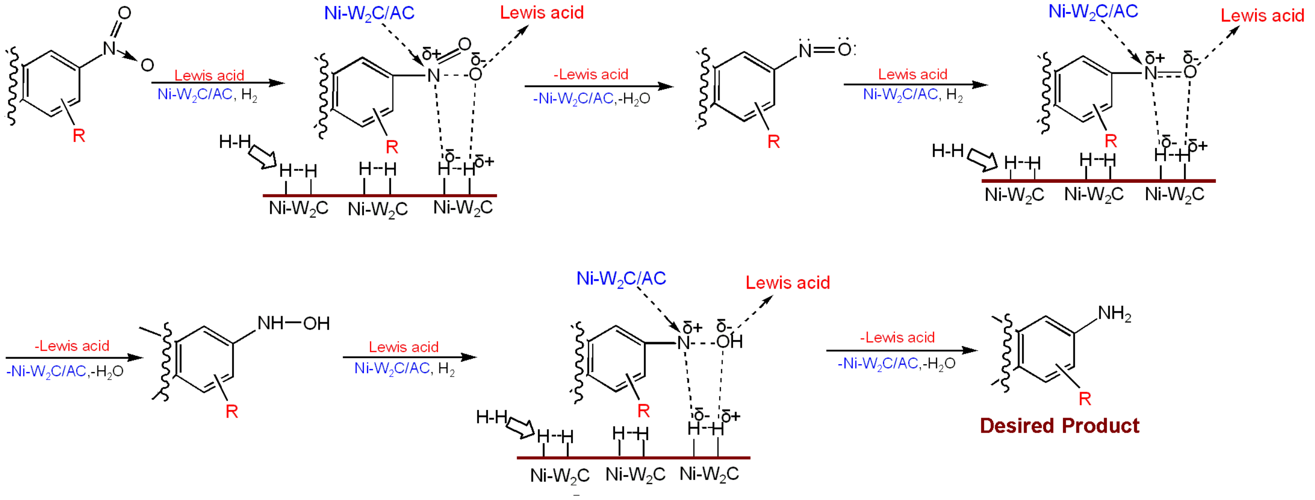

Scheme 2 Plausible mechanism of the dual activation in nitrobenzene hydrogenation by Ni-W$_2$C/AC and Lewis acid

reactions of nitrobenzene over Ni-W$_2$C/AC in the presence of Lewis acid like $FeCl_3$, $AlCl_3$ or $SnCl_2$ were performed, and the 100, 97 or 97.3% (Entry 2, 3 and 4, respectively, Table 2) of unexpectedly high yield with 100% selectivity can be obtained, which are significantly higher than those on Ni-W$_2$C/AC (52%, Entry 2 in Table 2) or only in the presence of $FeCl_3$ (9.2%, Entry 1 in Table 2), which suggests the existence of strong synergism between Lewis acid and Ni-W$_2$C/AC. According to the reported literatures, the iron complex catalysts may be efficient for hydrogenation of nitroarenes,[85] we investigated the catalytic performance of the catalytic systems containing Ni-W$_2$C/AC and non-Lewis acidic $Fe(NO_3)_3$ (or $FeCl_2$), but only 64 or 74% of yield can be obtained, respectively. In combination of the above results, the unexpected synergism between Ni-W$_2$C/AC and Lewis acid especially $FeCl_3$ significantly enhances the cataytic hydrogenation of nitrobenzene. More interestingly, by using the catalytic system including Ni-W$_2$C/AC and $FeCl_3$, the aniline is the only product, no *p*-aminophenol can be detected, which challenges the long-held axiom that the combination of Lewis acid and hydrogenation catalyst mainly enhances the transformation of nitrobenzene (NB) to *p*-aminophenol under hydrogenation conditions. That is to say, by using the developed Ni-W$_2$C/AC catalyst, the addition of Lewis acid notably enhances the chemoselective hydrogenation of nitro group, but not Bamberger rearrangement of the formed intermediate PHA.

A plausible reaction mechanism is proposed (Scheme 2). Metal carbide is most active catalyst for hydrogen-concerned reactions,[51-54] Ni-W$_2$C/AC can activate H_2 to produce active H for the reaction. The Lewis base (Ni-W$_2$C/AC)[53,54] and acid ($FeCl_3$) may interact with the substrate and the intermediates to weaken the NO_2, N=O and N-O bonds (can be illustrated by the peak shift in the FTIR, Fig. S1), and then they are hydrogenated by the active H. As a result, the chemsoselective hydrogenation of nitroarenes can be efficiently enhanced by the catalytic systems containing Ni-W$_2$C/AC catalyst and Lewis acid. From our previous report,[60] it can be proposed that the NSB and PHA are possible intermediates in the reduction process of nitrobenzene by Lewis acid promoted Ni-W$_2$C/AC catalytic system. In details, firstly, the N-O of NO_2 is activated by the coordination of Ni-W$_2$C/AC with N atom and the Lewis acid with O, and the activated H by Ni-W$_2$C/AC interacts with the actvated N-O bond, and as a result, the intermediate Ar-NO is formed. The Ni-W$_2$C/AC and Lewis acid synergistically catalyze the above porcess. Secondly, the Ar-NO is further activated and hydrogenated to Ar-NHOH, and then the formed Ar-NH-OH is further activated and hydrogenated to produce the final product Ar-NH_2 though the similar activation process as above. In order to further shed light on the above mechanism, the control experiments by 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 2 (Entries 8 and 9). The reaction results demonstrate that the aniline is the only product (Fig. S2-S4) for the nitrosobenzene, phenylhydroxylamine or nitrobenzene as substrate of chemoselective reduction. Correlated to the former meachanism analysis and reference, the control experimental results further confirm the above proposed reaction route for the chemoselective reduction of nitro group over the developed catalytic system containing Ni-W$_2$C/AC catalyst and Lewis acid in this work.

Scope of the substrates

To investigate the scope of the developed catalytic system in this work, the hydrogenation reactions of structurally diverse nitro compounds were performed, and the optimized reaction results are presented in Table 3. From Table 3, the Ni-W$_2$C/AC catalyst–Lewis acid system has excellent selectivity and yield for the hydrogenation of various functionalized nitroaromatics under the optimized reaction conditions. Interestingly, halogen substituted nitrobenzenes were reduced to corresponding chloroanilines in high yields and without any dehalogenation (Table 3, entries 4-6). The reducible functional groups in reaction substrates like OH, OCH_3, $COOC_2H_5$ and COOH remained totally unaffected under the reaction conditions (Table 2, entries 7-11). Notably, the hydrogenation reactions of nitroaniline also occurred selectively to give the corresponding diphenylamines with a 100% selectivity (Table 2, entries 12 and 13). The multiamino aromatic compounds, *o*-toluidine, *m*-toluidine, *p*-toluidine and nitronaphthalene, as key fragments in dyes can also be efficiently and selectively produced by the chemoselective

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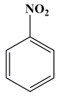
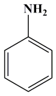
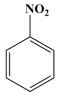
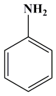
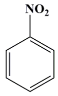
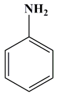
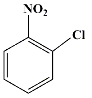
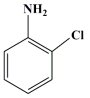
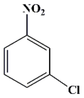
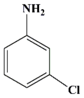
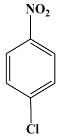
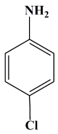
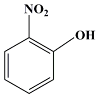
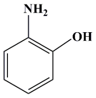
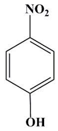
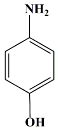
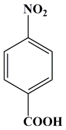
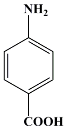
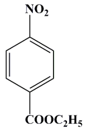
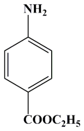
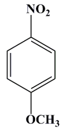
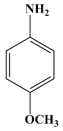
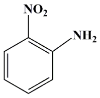
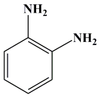
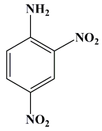
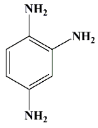
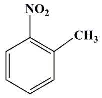
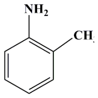
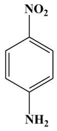
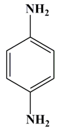
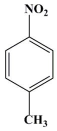
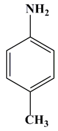
Table 3 Summary on the chemoselective Hydrogenation of substituted nitroarenes over the developed catalytic system containing Ni-W_2C/AC catalyst and Lewis acid.[a]

Entry	Substrate	Product	$FeCl_3$ (g)	P_{H2} (MPa)	*time* (h)	Sel./Yield (%)[b]
1			0.02	2.5	2.5	100/100
2			0.02	2.5	2.5	100/100[c]
3			0.02	2.5	2.5	100/99.5[d]
4[e]			0.04	3.0	5.0	99.5/98.5
5[e]			0.04	3.0	5.0	99/99.0
6[e]			0.04	2.8	4.0	100/100
7			0.05	3.2	5.0	100/100
8			0.06	3.2	5.0	100/100
9			0.04	3.2	5.0	100/100[b]
10[e]			0.04	3.0	5 .0	100/100
11			0.04	3.5	5.0	100/100
12			0.04	3.0	5.0	100/99
13			0.04	3.0	5.0	100/100
14			0.04	3.0	4.5	100/100
15			0.04	3.0	4.5	100/100
16			0.04	3.0	4.5	100/100

[a] Reaction conditions: 50 mg catalyst, 4.1 mmol substrates, T=240 °C; [b] detected by GC-MS and ^{1}H-NMR; [c] Scaled up by factor 10; [d] seperated yield for c; [e] T=220 °C.

hydrogenation of corresponding nitroarenes using Ni-W_2C/AC catalyst–Lewis acid system (Table 2, entries 14-18). The above results exhibit the developed Ni-W_2C/AC catalyst-Lewis acid system in this work is a promising catalyst for the clean and efficient production of functionalized arylamines via chemoselective hydrogenation reaction from their corresponding nitroarenes, the vulnerable moieties in the various substrates were well tolerated during the reaction process in this approach.

Scaled-up catalytic properties

As we all know that the scaled-up catalytic properties and isolated yield are very important for a practical catalyst, and thereby, using nitrobenzene as a probe substrate, the scaled-up experiment by factor 10 was performed, and the GC yield and isolated yield are presented in Table 3 (entries 2 and 3). Reaction results show that no difference in selectivity and GC yield take palce if the reaction is scaled-up by factor 10, as well as 99.5% of isolated yield can be obtained, which is very close to the GC yield. In our previous report,[60] it was found that the transition metal modified carbide on AC is so stable in the reduction systems that no leaching may be detected. In this work, without adding extra fresh catalyst, the seperated catalyst can be reused leaching of Ni or W is negligible. From above, the non-precious without loss in catalytic performance, and therefore we think the metal Ni-W_2C/AC catalysed chemsoselective hydrogenation could be a practical approach for the production of functionalized arylamines.

Recyclability

In industrialized production process, the catalyst recycling is definitely important in the heterogeneous catalytic reactions. Therefore, we investigated the recyclability of our developed

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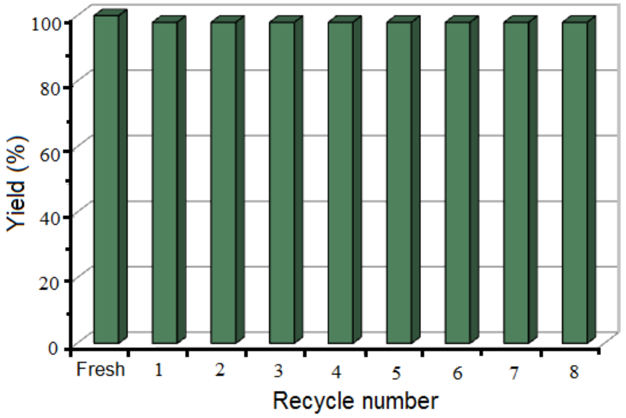

Fig. 3 Recyclability test of the develoepd 5%Ni25%W_2C/AC catalyst-Lewis acid catalytic system for chemoselective hydrogenation of nitrobenzene to yield aniline. Reaction conditions: 50 mg catalyst, 0.02 g $FeCl_3$, 4.1 mmol nitrobenzene, P_{H2}=2.5 MPa, T=240 °C, t=2.5 h.

catalytic for chemoselective hydrogenation reaction by using nitrobenzene as a model substrate. The seperated spent catalyst was used only by washing with solvent and drying before use, as well as no extra fresh catalyst was added. Figure 3 presents the experimental results for recycling eight times. From the reaction results, we can observe that the developed catalytic system containing Ni-W_2C/AC and Lewis acid can be reused by simply separation without losing its activity for more than eight runs of the used catalyst, and there is no loss in the yields of aromatic anilines, suggesting the potential catalyst for the chemoselective hydrogenation of nitroarenes in practical applications.

Conclusions

In summary, we present an interesting and practical approach for the clean synthesis of various functionalized arylamines from corresponding nitroarenes by the synergistically enhanced catalysis of Ni-W_2C catalyst and Lewis acid whose role is anomalous in our catalytic system, as the traditional catalytic hydrogenation of nitrobenzene is to produce phenylhydroxylamine (PHA) in acid medium and further rearrange to *p*-aminophenol (PAP), during the process of analyzing the final reaction mixture, no PAP was detected. Our developed catalytic system containing Ni-W_2C catalyst and Lewis acid demonstrated excellent catalytic properties, ascribing to the remarkably synergistic effect between Ni-W_2C catalyst and Lewis acid. Separation of the product from the catalyst–Lewis acid system is simple, and the catalytic system can be reused directly. This catytic system has great potential for industrial application. In view of the importance of functionalized arylamines in the industrial manufacture. The developed catalytic system in this work, once complete developed, may open an avenue 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. This approach can provide some guidance of developing Lewis acid promoted catalytic systems in the other applications.

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