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Synergistic effect from Lewis acid and the Ni-W$_2$C/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$_2$C/AC and Lewis acid is presented.
Synergistic effect from Lewis acid and the Ni-W₂C/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 synthesis of various functionalized arylamines from their corresponding substituted nitroarenes through the unexpected synergistic effect of Lewis acid and Ni-W₂C/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 FeCl₃-Ni-W₂C/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 FeCl₃-Ni-W₂C/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 catalysts 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.²⁻⁶⁻⁴⁻⁴ 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.⁷ 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 replacing 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...
and surface physicochemical properties, 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. 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-tolerance stability, and the possible metal-support interaction. 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, 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. 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. From the reference, the existence of CO 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. Due to the weak basic properties of metal carbide, 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-W2C/AC catalyst which was pretreated by calcination in Ar at 300°C and then was reduced with a 10 vol.% H2/Ar mixture (30 ml min-1) at 40°C for 60 min and then was cooled 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. 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-W2C/AC and the combined Lewis and Ni-W2C/AC system (after suffering from reaction temperature and pressure but not adding H2) were collected with the same spectrometer, as well as the FTIR spectra of pure liquids containing NB, NSB or PHA.
respectively were also collected for comparison.

**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 Chemicals Corp., Ltd) and 4.1 mmol of nitrobenzene (Tianjin Beilian Fine Chemicals Corp., Ltd), and the desired amount of Lewis acids were put into the reactor and purged 3 times with N₂ to replace the air in the reactor and purged 3 times with H₂ to replace the N₂ 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 H₂ 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 separated 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 separated 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 (Mo₂C and W₂C) and the modified W₂C (M-W₂C/AC, M= Fe, Co, Ni and Cu) catalysts on AC according to the reported carbothermal reduction method. 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 W₂C 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 WC or WC, implying no obvious insertion of transition metal into metal carbide matrix. The supported W₂C catalyst on AC can be prepared via carbothermal reduction method. We performed the H₂-TPR experiments on the oxide state precursors of the diverse transition metals modified supported W₂C catalysts to investigate the effect of the addition of transition metals on the redox of supported WO₃ 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 transition 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 WOₓ 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 H₂ dissociation to assist the reduction of WOₓ. As a result, the formation of W₂C and WC phases was enhanced, consistent with the previous reports. This promoting process can be further proved by the XRD in Fig. 1A, and the more sharp and strong
peaks towards carbide on the modified W$_2$C/AC than on the unmodified one can be observed, suggesting that the addition of transition metals doesn’t change the dispersity of W$_2$C 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. This kind of promoting effect can efficiently improve the catalytic performance of supported W$_2$C 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$_2$ dissociation. That is to say, the addition of transition metals, especially Ni can synergistically promote the W$_2$C/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 or phenylhydroxylamine intermediates. From Table 1, it can be observed that the supported metal carbide catalysts on AC, especially Ni modified W$_2$C/AC are 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$_2$C/AC in this transformation. 25% of optimal W$_2$C 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. According to the previous reports, Fe, Co, Ni are active catalysts for the hydrogenation of nitrobenzene, although the selectivity is not satisfactory, as well as the Fe, Co and Ni are demonstrated to promote the formation of molybdenum carbides, which suggest the possibility of synergistic interaction between Fe, Co or Ni and Mo$_2$C. Therefore, we added some transition metals and investigated the promoting effect on the Mo$_2$C/AC catalyst. Interestingly, we illustrate 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 yield. In order to elucidate the promoting effect of the added Ni on the catalytic performance of the supported W$_2$C catalyst on AC for the chemoselective hydrogenation of nitroarenes, the two samples 25% W$_2$C/AC and 5% Ni/AC were also tested. In comparison of the 25% W$_2$C/AC or 5% Ni/AC, the incorporated catalyst (5% Co-25% W$_2$C/AC) exhibits unexpectedly better catalytic activity, even much better than the physically mixed 25% W$_2$C/AC or 5% Ni/AC, implying the existence of synergistic effect between Ni and W$_2$C for chemoselective hydrogenation.

Through adding Ni into W$_2$C/AC catalyst, the catalytic performance of supported carbide catalyst has been notably improved. However, the only 52% of yield can be obtained. The improvement in catalytic activity of Ni-W$_2$C/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. We proposed the addition of Lewis acid into the hydrogenation reaction systems over Ni-W$_2$C/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$_2$C/AC catalyst can be successfully established, the concept for Lewis acid promoting Bamberger rearrangement of the formed intermediate phenylhydroxylamine (PHA) in process of catalytic hydrogenation of nitrobenzene to produce p-amino phenol but not aniline was broken.

Under the same conditions, the catalytic hydrogenation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Sel./Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>100/4.9</td>
</tr>
<tr>
<td>2</td>
<td>AC</td>
<td>100/4.9</td>
</tr>
<tr>
<td>3</td>
<td>25%Mo$_2$C/AC</td>
<td>100/17.3</td>
</tr>
<tr>
<td>4</td>
<td>25%W$_2$C/AC</td>
<td>100/35.0</td>
</tr>
<tr>
<td>5</td>
<td>15%W$_2$C/AC</td>
<td>100/22.0</td>
</tr>
<tr>
<td>6</td>
<td>20%W$_2$C/AC</td>
<td>100/28.0</td>
</tr>
<tr>
<td>7</td>
<td>30%W$_2$C/AC</td>
<td>100/32.0</td>
</tr>
<tr>
<td>8</td>
<td>5%Fe$_2$5%W$_2$C/AC</td>
<td>100/43.7</td>
</tr>
<tr>
<td>9</td>
<td>5%Co$_2$5%W$_2$C/AC</td>
<td>100/45.0</td>
</tr>
<tr>
<td>10</td>
<td>5%Ni$_2$5%W$_2$C/AC</td>
<td>100/52.0</td>
</tr>
<tr>
<td>11</td>
<td>5%Cu$_2$5%W$_2$C/AC</td>
<td>100/39.7</td>
</tr>
<tr>
<td>12</td>
<td>3%Ni$_2$5%W$_2$C/AC</td>
<td>100/36.0</td>
</tr>
<tr>
<td>13</td>
<td>4%Ni$_2$5%W$_2$C/AC</td>
<td>100/48.4</td>
</tr>
<tr>
<td>14</td>
<td>6%Ni$_2$5%W$_2$C/AC</td>
<td>100/50.7</td>
</tr>
<tr>
<td>15</td>
<td>7%Ni$_2$5%W$_2$C/AC</td>
<td>100/47.0</td>
</tr>
<tr>
<td>16</td>
<td>5%Ni/AC</td>
<td>100/19.0</td>
</tr>
<tr>
<td>17</td>
<td>5%Ni/AC+25%W$_2$C/AC</td>
<td>100/42.0</td>
</tr>
</tbody>
</table>

* Reaction conditions: 50 mg catalyst, 4.1 mmol nitrobenzene, P$_{H2}$=2.5 MPa, T=240 °C, t=2.5 h; * detected by GC-MS and $^1$H-NMR.

**Table 2 Hydrogenation of nitrobenzene over 5%Ni-25%W$_2$C/AC catalysts with and without the addition of different promoting additives.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additives</th>
<th>Sel./Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/92</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5%Ni$_2$5%W$_2$C/AC</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/52.0</td>
</tr>
<tr>
<td>3</td>
<td>Anhydrous AlCl$_3$</td>
<td>100/97.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Anhydrous SnCl$_4$</td>
<td>100/97.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Anhydrous (NO$_2$)$_2$</td>
<td>100/64.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/74.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/100$^a$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5%Ni$_2$5%W$_2$C/AC</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/100$^a$</td>
</tr>
<tr>
<td>9</td>
<td>Anhydrous FeCl$_3$</td>
<td>100/100$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 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; * detected by GC-MS and $^1$H-NMR; ** the nitrosobenzene and phenylhydroxylamine being used as substrates, respectively.
Scheme 2 Plausible mechanism of the dual activation in nitrobenzene hydrogenation by Ni-W_{x}C/AC and Lewis acid

reactions of nitrobenzene over Ni-W_{x}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_{x}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_{x}C/AC. According to the reported literatures, the iron complex catalysts may be efficient for hydrogenation of nitroarenes, we investigated the catalytic performance of the catalytic systems containing Ni-W_{x}C/AC and non-Lewis acidic Fe(NO_{3})_{3} (or FeCl_{3}), but only 64 or 74% of yield can be obtained, respectively. In combination of the above results, the unexpected synergism between Ni-W_{x}C/AC and Lewis acid especially FeCl_{3} significantly enhances the catalytic hydrogenation of nitrobenzene. More interestingly, by using the catalytic system including Ni-W_{x}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_{x}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. Ni-W_{x}C/AC can act as activator for the reaction. The Lewis base (Ni-W_{x}C/AC) 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 activated H by Ni-W_{x}C/AC interacts with the activeted N-O bond, and as a result, the intermediate Ar-NO is formed. The Ni-W_{x}C/AC and Lewis acid synergistically catalyze the above process. Secondly, the Ar-NO is further activated and hydrogenated to Ar-NHOOH, 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 phenyldihydroxylamine 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, phenylhydroxyamine or nitrobenzene as substrate of chemoselective reduction. Correlated to the former mechanisation 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_{x}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_{x}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} 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 nitrinapthalene, as key fragments in dyes can also be efficiently and selectively produced by the chemoactive
Table 3 Summary on the chemoselective Hydrogenation of substituted nitroarenes over the developed catalytic system containing Ni-W\(_2\)C/AC catalyst and Lewis acid.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>FeCl(_3) (g)</th>
<th>(P_{H2}) (MPa)</th>
<th>time (h)</th>
<th>Sel./Yield (%)(^b)</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>0.02</td>
<td>2.5</td>
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<td>100/100</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>0.02</td>
<td>2.5</td>
<td>2.5</td>
<td>100/100(^c)</td>
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<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.02</td>
<td>2.5</td>
<td>2.5</td>
<td>100/99.5(^d)</td>
</tr>
<tr>
<td>4(^e)</td>
<td></td>
<td></td>
<td>0.04</td>
<td>3.0</td>
<td>5.0</td>
<td>99.5/98.5</td>
</tr>
<tr>
<td>5(^e)</td>
<td></td>
<td></td>
<td>0.04</td>
<td>3.0</td>
<td>5.0</td>
<td>99/99.0</td>
</tr>
<tr>
<td>6(^e)</td>
<td></td>
<td></td>
<td>0.04</td>
<td>2.8</td>
<td>4.0</td>
<td>100/100</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>0.05</td>
<td>3.2</td>
<td>5.0</td>
<td>100/100</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>0.06</td>
<td>3.2</td>
<td>5.0</td>
<td>100/100</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>0.04</td>
<td>3.2</td>
<td>5.0</td>
<td>100/100(^f)</td>
</tr>
<tr>
<td>10(^f)</td>
<td></td>
<td></td>
<td>0.04</td>
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<td>12</td>
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<td></td>
<td>0.04</td>
<td>3.0</td>
<td>5.0</td>
<td>100/99</td>
</tr>
</tbody>
</table>

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

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 place 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,\(^6\) 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 without loss in catalytic performance, and therefore we think the metal Ni-W\(_2\)C/AC catalysed chemoselective 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...
precious metal catalysts with less expensive transition metal phenylhydroxylamine (PHA) in acid medium and further separation without losing its activity for more than eight runs of the used catalyst, and there is no loss in the yields of aromatic chemicals from nitro groups. In addition, the substitution of avenue for the production of valuable amine-containing 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.

Conclusions

In summary, we present an interesting and practical approach for the synthesis of various functionalized arylamines from corresponding nitroarenes by the synergistically enhanced catalysis of Ni-W/C catalyst and Lewis acid whose role is anomalous in our catalytic system, as the traditional catalytic hydrogenation of nitrobenzene is catalytic for chemoselective hydrogenation reaction by using nitrobenzene as a model substrate. The separated 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/C 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.

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Notes and references