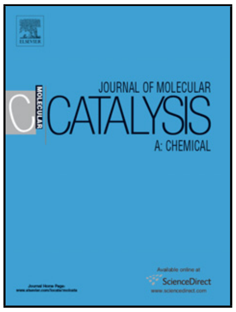

Title: Ni-W_2C/mpg-C_3N_4 as a promising catalyst for selective hydrogenation of nitroarenes to corresponding aryl amines in the presence of Lewis acid

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Ni-W_2C/mpg-C_3N_4 as a promising catalyst for selective hydrogenation of nitroarenes to corresponding aryl amines in the presence of Lewis acid

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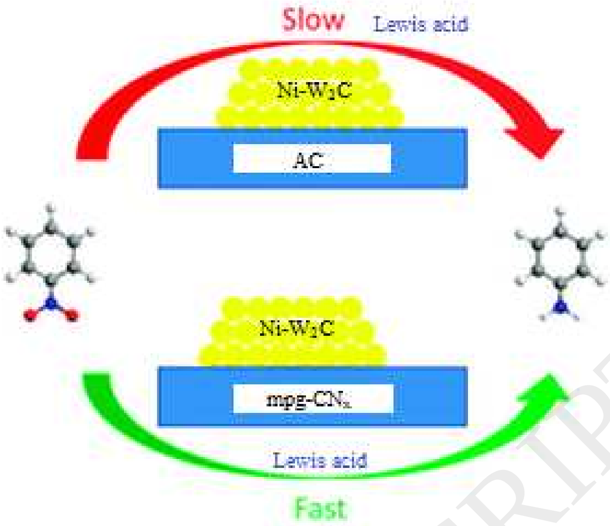
Highlights

- Ni-W_2C/mpg-C_3N_4 shows promising catalytic properties for selective hydrogenation.
- The superior catalytic properties are ascribed to synergism of catalyst/Lewis acid.
- The mpg-C_3N_4 efficiently strengthens the synergism between catalyst and Lewis acid.
- Support type notably affects the dispersion and reducibility of supported NiO-WO_x.
- Ni-W_2C/mpg-C_3N_4 can be a practical catalyst for synthesis of diverse

arylamines.



Graphical abstract

Abstract

The selective hydrogenation of nitroarenes to their corresponding aryl amines has been investigated over the supported nickel propoted tungsten carbide catalyst on polymeric mesoporous graphitic carbon nitride (Ni-W_2C/mpg-C_3N_4) in the presence of Lewis acid. The Ni-W_2C/mpg-C_3N_4 is demonstrated much higher catalytic activity and selectivity for the selective hydrogenation of nitrobenzene than the supported Ni-W_2C catalyst on activated carbon (Ni-W_2C/AC) and mesoporous carbon (Ni-W_2C/CMK-3), and the developed Ni-W_2C/mpg-C_3N_4 aslo exhibits excellent catalytic properties for the selctive hydrogenation of various substrates comprising the extra reducble functionalized groups besides nitro group to diverse functionalized arylamines, industrially improtants compounds, offering more than 92% of yield with 100% selectivity, which may be ascribed to the strengthened mass transfer by using mesoporous support, intentified synergistic effect between Ni-W_2C/mpg-C_3N_4 and

Lewis acid owing to the basicity of mpg-C_3N_4, as well as the improved reducibility of NiO-WO_3 and the dispersion of Ni-W_2C. It can be also found that the developed catalyst could be easily recovered by filtration and recycled many times without visible loss in its catalytic performance. The significantly improved catalytic properties of supported Ni-W_2C catalyst fabricated by using mpg-C_3N_4 as a superior carrier in the presence of Lewis acid allows it to be a promising candidate for the clean and highly-efficient synthesis of diverse functionalized arylamines through the selectivie hydrogenation of substituted nitroarenes.

Keywords: Selective hydrogenation; Metal carbide; Support effect; mpg-C_3N_4; Aryl amines

1. Introduction

Aryl amines, as the key intermediates for fine chemical, agrochemical, and pharmaceutical industries [1-3], are generally produced by the selective hydrogenation of nitroarenes [4-9]. However, selective hydrogenation of the extra reducible moieties-containing nitroarenes remains challenging. 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 broadly employed [10-13], although they show high activity and selectivity for nitrobenzene hydrogenation, the selectivity towards the hydrogenation of many functionalized nitroarenes, especially chloronitrobenzene, still remains quite low owing to the co-existing dehalogenation reaction in the hydrogenation process. On the other hand, platinum, rhodium and ruthenium based catalysts have also been extensively investigated [14-18], they have shown fascinating catalytic performance under mild reaction conditions, but they are still not suitable for an industrial application due to their high cost and very limited availability.

Recently, the transition-metal carbides, especially molybdenum carbide and tungsten carbide**,** as Pt-like metals have attracted much attention as promising material for their outstanding bulk and surface physicochemical properties [19,20], therefore it’s a promising approach to employ transition metal carbide catalyst in the hydrogenation of nitroarenes with excellent activity and high selectivity. According to the reported literatures that transition metal carbide had been attempted as additives or supports for precious metal catalysts to catalyze the hydrogenation of nitroarenes using hydrazine hydrate as a hydrogen source, but the usage of precious metals is indispensable [21,22]. 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 [23-27]. In our precious report, we have employed supported transition metal molybdenum carbide catalysts in the hydrogenation of functionalized nitroarenes using hydrazine hydrate as hydrogen source [28], therefore, transition metal carbide has great potential for the hydrogenation of nitroarenes under the condition of hydrogen. From the viewpoint of economic and clean process, the replacement of hydrazine hydrate by hydrogen is highly desirable.

We previously demonstarted that the supported Ni-W_2C catalyst on AC can be promising candidate for selective hydrogenation of diverse nitroarenes to their coppesponding aryl amines by using hydrogen to replace hydrazine hydrate as H source, and also the promoting effect of the synergism between the Ni-W_2C (Lewis base) and Lewis acid on the reaction was established [10]. However, the relatively high reaction temperature and pressure is indispensible to obtain satisfactory reaction results. To develop highly efficient and highly selective catalytic systems for aryl amine production under relatively low reaction and presure is highly desirable, but it still remains challenge. mpg-C_3N_4 materials with two-dimension pore architecture possess higher specific surface area and larger pore volume, which results in enhanced catalytic performances in catalysis due to higher surface density of active sites exposed on the surface, their easier accessibility by strengthened diffusion, and the basicity [14,15,29-37]. Hopefully the offered base sites from mpg-C_3N_4 may strengthen the synergistic effect between the supported Ni-W_2C catalyst and Lewis acid that was established in our previous report [10].

In this work, the supported Ni-W_2C catalyst on mpg-C_3N_4 is firstly prepared and used in chemoselective hydrogenation of functionalized nitroarenes to their corresponding aryl amines in the presence of Lewis acid. The Ni-W_2C/mpg-CN_x catalyst shows fascinating catalytic properties, ascribed to the strengthened synergistic effect between the supported Ni-W_2C catalyst and the added Lewis acid, besides to the support effect on the dispersion of Ni-W_2C, the reducibility of NiO-WO_3 of the precursor of Ni-W_2C, as well as the improved mass transfer during catalysis owing to the well-ordered mesoporous structure of the mpg-C_3N_4 support. The possible meahcnism was also discussed. It can be also found that the developed catalyst could be easily recovered by filtration and recycled many times without visible loss in its catalytic performance. The improved catalytic properties of supported Ni-W_2C catalyst fabricated by using mpg-C_3N_4 as a superior carrier in the presence of Lewis acid allows it to be a promising and practical candidate for the clean and highly-efficient synthesis of diverse functionalized arylamines through the selectivie hydrogenation of substituted nitroarenes.

2. Experimental Section

2.1. *Preparation of catalysts*

Mesoporous silica SBA-15 powder was synthesized according to the previous paper [38,39]: In a typical synthesis, 4.0 g of Pluronic P123 purchased from Sigma-Aldrich Cor. was dissolved in 30 g of distilled water and 120 g of 2 M HCl solution under vigorous stirring. After the complete dissolution, 8.50 g of TEOS (Acros, Purity 98 %) was added into above solution. The mixture was further stirred at 35 ^{o}C for 20 h. The resulting mixture was aged at 80 °C overnight. The achieved solid product was recovered, washed, and then dried at 105 °C, followed by calcination at 500 °C for 6 h.

The mpg-C_3N_4 was prepared according to the reported procedure [40]: 0.5 g of calcined SBA-15 was added to a mixture of ethylenediamine (2.2 g) and carbon tetrachloride (5.4 g). The resultant mixture was refluxed and stirred at 90 °C for 6 h. Then, the dark-brown solid mixture was heated in a nitrogen flow at 600 °C to carbonize the polymer. The mesoporous carbon nitride was recovered after dissolution of the silica framework in 5 wt.-% hydrofluoric acid, followed by filtration, washing several times with ethanol, and drying at 105 °C. CMK-3 was also prepared as follows: Briefly, 1 g of calcined SBA-15 was added to a solution containing 1.25 g of sucrose, 0.14 g of H_2SO_4 and 5 g of H_2O. The mixture was placed in a drying oven for 6 h at 100 °C, and then the temperature was increased to 160 °C and kept this temperature for 6 h. The resultant solid, containing silica template, partially polymerized and carbonized sucrose, was treated again at 100 °C, and then at 160 °C using the same drying oven after the addition of the solution containing 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O. The carbonization was performed by pyrolysis in nitrogen atmosphere. The obtained carbon-silica composite was washed with 5 wt% HF at room temperature to remove the silica template. The template-free carbon product was obtained by filtering, washing with ethanol, and drying at 120 °C. The as-received activated carbon 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 Ni-W_2C/mpg-C_3N_4 (5% Ni and 25%W_2C) was prepared as follows: an aqueous solution of nickel nitrate and ammonium tungstate solution containing desired amount of Ni and W were impregnated onto the prepared mpg-C_3N_4 support using incipient wetness impregnation (IWI) method reported in literatures [41,42], followed by drying overnight and calcinating at a certain temperature in N_2 atmosphere to obtain NiO-WO_x/mpg-CN_x. Subsequently, the NiO-WO_x/mpg-C_3N_4 were carburized in CH_4/H_2 mixture according to references [43-46]. Finally, the Ni-W_2C/mpg-C_3N_4 catayst was obtained after it suffered from passivating in 1% O_2/N_2. For comparison, the two samples Ni-W_2C/CMK-3 and Ni-W_2C/AC were prepared by using the similar procedure as above except for the use of different support.

2.2. Characterization of catalysts

Nitrogen adsorption–desorption isotherms were measured at -196 °C using a Builder 4300 analyzer. The specific surface areas were calculated according to the Brunauer-Emmet-Teller (BET) method and the pore size distributions were calculated from an adsorption branch of the iotherm by the (Barrett-Joyner-Halenda) BJH method. X-ray diffraction patterns were collected from 10 to 80^o at a step width of 0.02^o 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. In a typical H_2-TPR experimental procedure, a quartz tube was loaded with 100 mg of sample which was pretreated by calcination in Ar at 300 ^oC 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 ^oC at a ramp rate of 10 ^oC min^{-1}.

2.3. Catalytic performance measurement

Catalytic measurements were performed according to the literature [10]: In a typical procudure, a certain amount of the as-prepared catalyst, cyclohexane as solvent (Tianjin Fuyu Chemials Corp., Ltd) and 4.1 mmol of nitrobenzene (Tianjin Beilian Fine Chemcials Corp., Ltd) were put into the in a 50 mL stainless steel autoclave batch reactorreactor 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 performed at the desired temperature and H_2 pressure under vigorous stirring (1000 rpm). After appropriate reaction time, the temperature was lowered quickly in an ice-water bath and the hydrogen pressure was released, then the catalyst systems including $FeCl_3$ were separated from the products by easily filtration, washed with cyclohexane, and then reused in the next cycle under the same reaction conditions. The filtrate and washing liquid were combined to obtain the mixture for chromatography analysis. The mixture was quantitatively analyzed by gas chromatography (GC) and liquid chromatography (LC). The molecular structures of the synthesized arylamines were confirmed by mass spectrometer (MS) and 1H NMR (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 added nitrobenzene.

3. Results and discussion

3.1. Characterization of catalyst

By using established procedure [47], we prepared the mpg-C_3N_4. The structure of the mpg-C_3N_4 support and the as-prepared Ni-W_2C/mpg-C_3N_4 catalyst were firstly characterized by X-ray diffraction analysis (XRD). The XRD patterns (Fig. 1a) indicate a characteric peak at 25.9 ^{o} of (002) packing of graphite-like carbon nitride [47]. The shaper and stronger peak corresponding to graphitic C_3N_4 on the XRD pattern of Ni-W_2C/mpg-C_3N_4 catalyst than that on the mpg-C_3N_4 can be clearly observed, ascribed to the further graphitization of the mpg-C_3N_4 support in the carburization procedure of supported NiO-WO_x precursor for preparing Ni-W_2C/mpg-C_3N_4 catalyst. Besides the diffraction peak at 25.9 ^{o} corresponding to mpg-C_3N_4, the XRD peaks of the Ni-W_2C/mpg-C_3N_4 at 34.2, 37.9, 39.3, 52.1, 61.7, 69.8, and 74.6 ^{o} were well resolved, assigned to the diverse planes of W_2C phases with hexagonal structure (JCPDS 20-1315), as well as the diffraction peaks at 31.4, 34.2, 48.2, 64.1, and 65.7 ^{o} in the XRD patterns can be assigned to the (001), (100), (101), (110), and (002) planes of WC crystal phase (JCPDS 03-1096),

respectively. Moreover, the three diffraction peaks at 27.2, 40.3 and 43.9 ^{o} can be clearly observed, asigned to WO_2, W, and Ni phases, repectively [28,48-50]. The above XRD results show the supported Ni and W_2C catalyst on mpg-C_3N_4 was successfully prepared [10,28], besides the existence of W and WO_2 phase on the catalyst. The BET technique was employed to investigate the textural properties of the catalysts, and the nitrogen adsorption-desorption isotherms are presented in Fig. 1b. The isotherm curves of mpg-C_3N_4 reveals a higher surafce area of 451.6 m^2 g^{-1} and some micropores of the parent mpg-C_3N_4. After supporting Ni-W_2C, the obvious change in isotherm towards Ni-W_2C/mpg-C_3N_4 catalyst can be observed, ascribed to the partial collapse of mpg-C_3N_4 framework at higher calcination temperature in the process of carburization of W_2C precursor or to the possible blocked pores by Ni-W_2C particles.

Furthermore, we investigate the effect of support type on the crystalline phases of supported Ni-W_2C and the reducibility of the supported NiO-WO_x, the precursor of Ni-W_2C, by performing the XRD characterization experiment of Ni-W_2C/mpg-C_3N_4, Ni-W_2C/CMK-3, and Ni-W_2C/AC samples at the same analytical conditions, as well as the H_2-TPR measurement on the NiO-WO_x/mpg-C_3N_4, NiO-WO_x/CMK-3, and NiO-WO_x/AC samples, respectively. The XRD patterns and H_2-TPR profiles are presented in Fig. S1 and S2, respectively. From Fig. S1, the support type have obvious influence on the dominant crystalline planes and crystalline size of the supported Ni-W_2C catalysts, and further about 30, 34, 37 nm average crystalline size of W_2C phase on the Ni-W_2C/mpg-C_3N_4, Ni-W_2C/CMK-3, and Ni-W_2C/AC, respectively, can be obtained (Table S1). The H_2-TPR profiles of the NiO-WO_x/mpg-C_3N_4, NiO-WO_x/CMK-3, and NiO-WO_x/AC samples reveals that the reducibility of the supported NiO-WO_x is affected by the support type, and the lower reducing temperature of NiO-WO_x/mpg-C_3N_4 allows it to be easily carbothermally reduced to Ni-W_2C, which may be one of the reasons for high catalytic performance of the Ni-W_2C/mpg-C_3N_4 for selective hydrogenation [10,28].

3.2. Effect of support type on the supported Ni-W_2C catalysts

We previously demnstrated that the supported Ni-W_2C catalyst on AC to be a promising candidate for the selective hydrogenation of nitroarenes in the presence of Lewis acid [10], but the catalytic activity is not high enough for commercial application, and the development of more efficient catalyst for this industrially important reaction is highly desirable. Herein, the selective hydrogenation of nitrobenzene to aniline was used as a probe reaction to investigate the effect of support type of supported Ni-W_2C catalysts. The reaction results are summarized in Table 1.

The results show that the catalytic performance of the supported Ni-W_2C catalyst are notably dependent on the support type. By using mesoporous carbon or carbon nitride as support, more than 60% of yield of aniline can be obtained at 220 ^{o}C of the lower reaction temperature. However, only 52% of yield can be obtained even if the reaction temperature is increased to 240 ^{o}C. In conbination of reaction results with characterization results shown as above, the strengthened mass transfer by using mesoporous support, as well as the improved reducibility of NiO-WO_3 and the dispersion of Ni-W_2C of the Ni-W_2C/mpg-C_3N_4 makes it a superior catalyst for the desired reaction. Furthermore, the yield is dramatically increased from 73 up to 100% at 220 ^{o}C for 2.5 h by introducing Lewis acid $FeCl_3$ into the reaction systems, ascribed to the strengthened synergistic effect between Ni-W_2C/mpg-C_3N_4 and Lewis acid [10,40,47]. Furthermore, the compared results of the supported Ni-W_2C catalysts on diverse supports demonstrate that the support type and structure have significant influence on their catalytic performance. Among the three supported catalysts, the Ni-W_2C/mpg-C_3N_4 shows the best catalytic performance for the catalytic hydrogenation of nitrobenzene in the presence of $FeCl_3$, possibly ascribed to both the enhanced synergism between Ni-W_2C/mpg-C_3N_4 catalyst and Lewis acid by the alkalinity of support, besides the strengthened mass trasferring by the use of mesoprous support.

3.3. Possible reaction mechanism

A plausible reaction mechanism for the strengthened synergistic is proposed as Fig. 2. In our previously report [10], the synergistic effect from the Lewis acid and the Ni-W_2C/AC with weak basicity was established. mpg-C_3N_4 has been used as excellent base catalysts for diverse reactions [40,47]. Metal carbide is most active catalyst for hydrogen-concerned reactions [19-22], Ni-W_2C/AC can activate H_2 to produce active H for the reaction. The Lewis base (Ni-W_2C/mpg-C_3N_4) [21,22] and acid ($FeCl_3$) may interact with the substrate and the intermediates to weaken the NO_2, N=O and N-O bonds, 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_2C/mpg-C_3N_4 catalyst and Lewis acid. In details, firstly, the N-O of NO_2 is activated by the coordination of Ni-W_2C/mpg-C_3N_4 with N atom and the Lewis acid with O, and the activated H by Ni-W_2C/mpg-C_3N_4 interacts with the actvated N-O bond, and as a result, the intermediate Ar-NO is formed. The Ni-W_2C/mpg-C_3N_4 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. Owing to the application of basic mpg-C_3N_4, the synergism between supported Ni-W_2C catalyst and Lewis acid would be stengthened, and therefore, the improved catalytic performance can eb achieved.

3.4. Scope of the substrates

From above, the catalytic systems comprising Ni-W_2C/mpg-C_3N_4 and Lewis acid with the improved catlytic performance in selective hydrogenation of nitrobenzene to aniline has been primarily established, and herein, the scope of the developed catalytic system is investigated by performing catalytic hydrogenation of diverse nitroarenes with extra reducible groups under their optimized reaction conditions. The reaction results are sumarrized in Table 2.

From Table 2, the developed Ni-W_2C/mpg-C_3N_4 catalyst demonstrates excellent catalytic properties for the diverse substrates in the presence of Lewis acid, and many etra reducible substitued groups-containing aromatic amine compounds can be obtained with the 100% of high selectivity at 210-220 ^oC of lower temperature [10]. More interesting point is that the halogen substitued nitrobenzenes are selectively hydrogenated into their corresponding chloroanilines in a high yield and without any dehalogenation (Table 2, Entries 2-4, 13). The reaction results indicate that the developed Ni-W_2C/mpg-C_3N_4 is a much superior catalyst for selective hydrogenation of extensive scope of nitroarenes than the previosuly established Ni-W_2C/AC catalyst. The new catalytic system comprised of Ni-W_2C/mpg-C_3N_4 and Lewsi acid could be considered as a fascinating approach for efficient and selective hydrogenation of many nitroarenes and even extra reducible groups containing nitroaromatic substrates for the clean production of the industrially significant functionalized aromatic amines.

3.5. The large-scale catalytic transformtion

As an industrially important process, the scaled-up catalytic properties and isolated yield are essential. Therefore, by 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. 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 99.3% of isolated yield can be achieved, which is very close to the GC yield.

3.6. The resuability of the catalyst

In industrialized production process, the catalyst recovery and recycling is definitely significant. Therefore, we investigated the recyclability of our developed catalytic system for chemoselective hydrogenation by using nitrobenzene as a model substrate. In our previous report [28], it was found that the transition metal modified carbide on AC is so stable in the reduction systems that no leaching may be detected. Thereore, the seperated spent catalyst was used only by washing with solvent and drying before use, but without extra fresh catalyst being added. Figure 3 presents the reaction results for eight times' recycling. 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.

4. Conclusion

In summary, we develop a novel and efficient Ni-W_2C/mpg-C3N4 catalyst for selective hydrogenation of diverse nitroarenes in the presence of Lewis acid, which demonstrates much superior catalytic performance. be ascribed to the strengthened mass transfer by using mesoporous support, intentified synergistic effect between

Ni-W_2C/mpg-C_3N_4 and Lewis acid owing to the basicity of mpg-C3N4, as well as the improved reducibility of NiO-WO_3 and the dispersion of Ni-W_2C. It can be also found that the developed catalyst could be easily recovered by filtration and recycled many times without visible loss in its catalytic performance. The improved catalytic properties of supported Ni-W_2C catalyst fabricated by using mpg-C_3N_4 as a superior carrier in the presence of Lewis acid allows it to be a promising candidate for the clean and highly-efficient production of many industrially important functionalized arylamines through the selectivie hydrogenation of their correspnding substituted nitroarenes.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.xx.xxx.

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Figures and Tables:

Fig. 1 XRD patterns (a) and nitrogen adsorption-desorption isotherms (b) of the as-prepared Ni-W_2C/mpg-C_3N_4 catalyst and mpg-C_3N_4 carrier.

Fig. 2 Plausible mechanism of the selective hydrogenation of nitrogen to aniline over the Ni-W_2C/mpg-C_3N_4 catalyst in the presence of Lewis acid.

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, 4.1 mmol nitrobenzene, P_{H2}=2.5 MPa, T=220 ^{o}C, t=2.5 h.

Table 1 Catalytic performance of the supported Ni-W_2C catalysts on the diverse supports for selective hydrogenation of nitrobenzene.

Entry	Catalyst	Lewis acid	Conversion (%)	Selectivity (%)
1	Ni-W_2C/mpg-CN_x		73	100
2	Ni-W_2C/CMK-3	$FeCl_3$	60	100
3[a]	Ni-W_2C/AC	$FeCl_3$	52	100
4	Ni-W_2C/mpg-CN_x	$FeCl_3$	100	100
5	Ni-W_2C/AC		79	100
6	Ni-W_2C/CMK-3		88	100

Reaction conditions: 50 mg catalyst, 0.5g nitrobenzene, P_{H2}=2.5 MPa, T=220 ^{o}C, t=2.5 h. [a] From reference, T=240 ^{o}C [10].

Table 2 Catalytic performance of the Ni-W_2C/mpg-C_3N_4 catalyst for selective hydrogenation of diverse nitroarenes.

Entry	Substrate	Product	P_{H2} (MPa)	*Time* (h)	Conversion (%)	Selectivity (%)

1			2.5	2.5	100	100
2[a]			3.0	6.0	100	100
3[a]			3.0	6.0	98	100
4[a]			3.0	6.0	92	100
5			3.0	6.0	100	100
6[a]			3.5	5.5	98	100
7[a]			3.0	6.0	100	100
8[b]			3.0	5 .0	98.2	100
9[a]			3.0	6.0	100	100
10			3.0	6.0	100	100
11			3.0	6	100	100
12			3.0	6	94	100
13			3.0	6	100	100

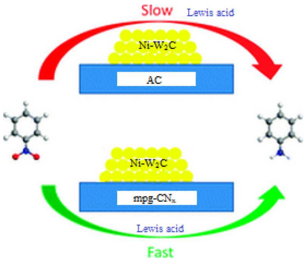
Reaction conditions: 50 mg catalyst, 4.1 mmol substrates, 0.02 g $FeCl_3$; T=220 °C; [a]T=210 °C; [b]T=215 °C.

Table 3 Catalytic performance of the Ni-W_2C/mpg-C_3N_4 catalyst for the large scale selective hydrogenation of nitrobenzene and the isolated yield.

Entry	Substrate	Product	P_{H2} (MPa)	*Time* (h)	Conversion (%)	Selectivity (%)
1			2.5	2.5	100	100

2[a]	2.5	2.5	100	100
3	2.5	2.5	99.3[b]	100

Reaction conditions: 50 mg catalyst, 4.1 mmol substrates, 0.02 g $FeCl_3$; T=220 °C; [a] Scaled up by factor 10; [b] separated yield for a.



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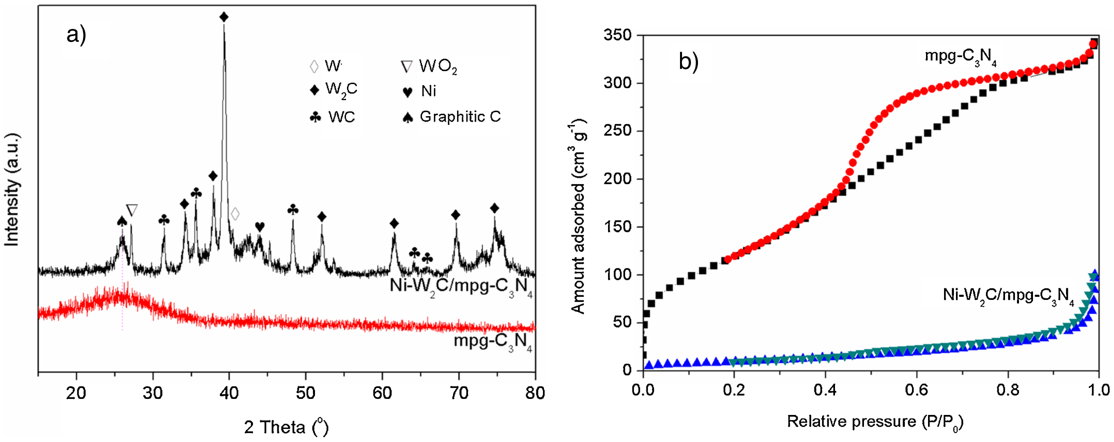
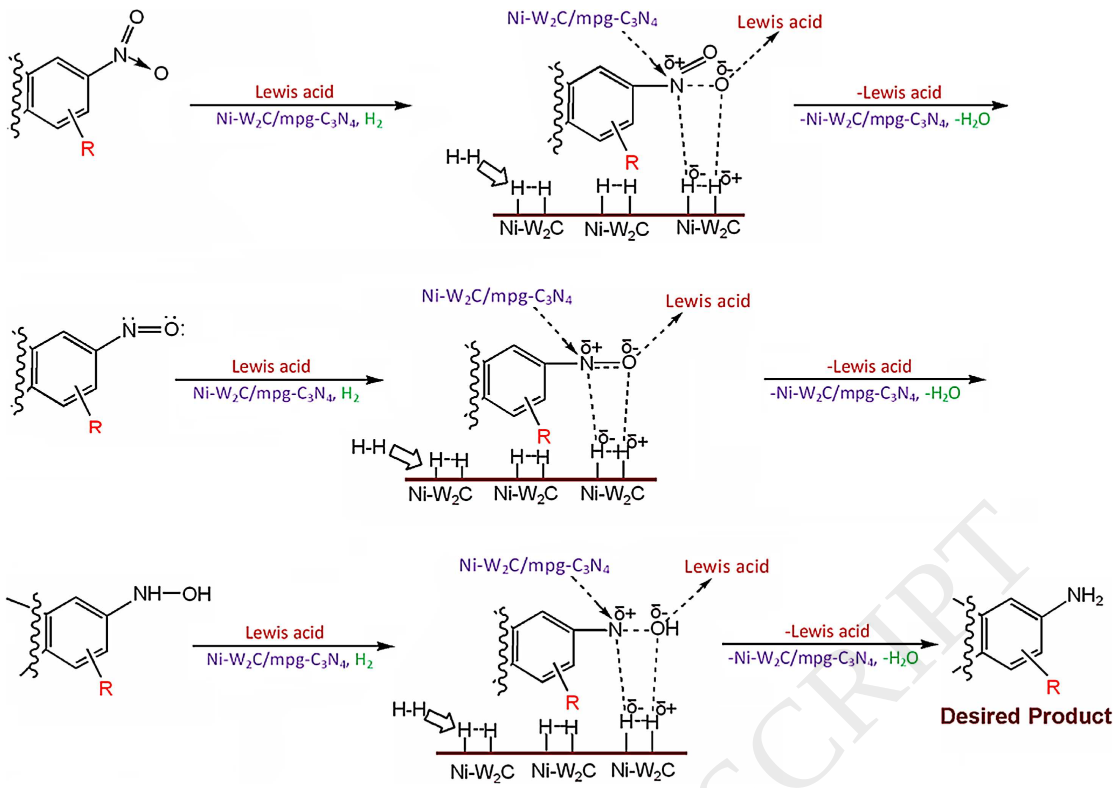
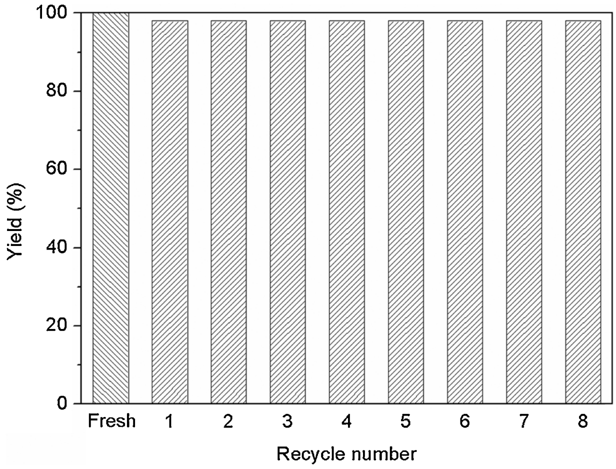

a)
◊ W
▽ WO$_2$
◆ W$_2$C
♥ Ni
♣ WC
♠ Graphitic C
Intensity (a.u.)
Ni-W$_2$C/mpg-C$_3$N$_4$
mpg-C$_3$N$_4$
20
30
40
50
60
70
80
2 Theta (°)
b)
350
300
250
200
150
100
50
0
Amount adsorbed (cm^3 g^{-1})
mpg-C$_3$N$_4$
Ni-W$_2$C/mpg-C$_3$N$_4$
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure (P/P$_0$)

gr1 .


Lewis acid
Ni-W$_2$C/mpg-C$_3$N$_4$, H$_2$
-Lewis acid
-Ni-W$_2$C/mpg-C$_3$N$_4$, -H$_2$O
Ni-W$_2$C/mpg-C$_3$N$_4$
H-H
Ni-W$_2$C
R
Desired Product

gr2 .



gr3 .