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# Activated carbon supported bimetallic catalysts with combined catalytic effects for aromatic nitro compounds hydrogenation under mild conditions



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# ABSTRACT

Non-noble nickel catalysts have been widely studied and tried in hydrogenation, however the problem of nickel particle sintering is more and more common in high-loaded nickel catalysts. A series of highly dispersed bimetallic Ni-M/AC (M = Cu, Co, Fe or Zn) catalysts were prepared by incipient wetness impregnation methods and applied in 1-nitronaphthalene hydrogenation to 1-naphthylamine under mild reaction conditions. The prepared catalysts were characterized by XRD, BET, H2-TPR, TEM, HRTEM, HAADF-STEM, XPS, ICP, FT-IR and H<sub>2</sub> chemisorption. The results show that the introduction of the metal promoter inhibits the sintering of the nickel and enhances the reducibility of the catalysts, leading to higher ratio of effective Ni° on the surface of the support, especially for Ni-Zn/AC sample. Moreover, the results of XPS indicate that the electron donating effect of Cu promoter increases surface electronic density of Ni, as a result, the electron-rich Ni might be produced because of the interfacial electronic effect, which favors the desorption and further impedes the hydrogenation of N-naphthylhydroxylamine. Ni-Zn/AC-350 with smaller nickel particles, better dispersion and larger content of effective Ni° presents the best catalytic performance in 1-nitronaphthalene hydrogenation to 1-naphthylamine under mild reaction conditions, it gives 100% conversion of 1-nitronaphthalene and 96.82% selectivity to 1naphthylamine under 0.6 MPa and 90°C for 5 h. Additionally, superior performances are also obtained in hydrogenation reactions of nitrobenzene, chloronitrobenzene, 1,5-dinitronaphthalene and 1,8-dinitronaphthalene over Ni-Zn/AC catalysts. With good hydrogenation activity the catalyst shows, the application prospect in industrial production of aromatic amine from aromatic nitro compounds has been becoming more and more extension.

# 1. Introduction

Aromatic nitro compounds are one of the most beautiful raw materials in the organic synthesis industry [1]. It can be reduced to aromatic amines, which are intermediates of various industrial reaction, such as the synthesis reaction of dyes and pigments, rubber antioxidants, pesticides, bio-chemicals and pharmaceuticals [2–8]. The traditional method for aromatic amines preparation is the reduction of aromatic nitro compounds, which is catalyzed by metal powder or alkali sulfide [9]. Unfortunately, it has such disadvantages as low yield, a large amount of waste water and residue [10]. Some researches were concerned with the production of aromatic amines by direct reduction of the corresponding aromatic nitro compounds [11–15]. Despite the considerable achievements that have been made, these catalytic systems are unfortunately associated with environmental issues and the formation of massive undesired by-products due to the use of stoichiometric reducing agents, such as NaBH<sub>4</sub> or hydrazine hydrate [16]. Hence, many researchers are focused on new method of liquid phase catalytic hydrogenation to prepare aromatic amines over supported noble and non-noble metal catalysts. Various supported noble metal nanoparticles of Pd [17–19], Ru [20,21], Ag [22], Au [23–25] and Pt [26] were applied in the hydrogenation reaction of aromatic nitro compounds to aromatic amines and presented perfect catalytic performance. However, these noble metal catalysts have the problems of high cost, scarce resources and un-stability, which restrict their extensive application in industry. Many researches have been contributed to exploit the catalytic hydrogenation of aromatic nitro compounds to corresponding amines over non-noble metal catalysts such as Raney Ni, Co-Mo-S, NiFeP and Ni-B amorphous alloys [27–32]. However, it requires large loading amount of metals or the reaction must be carried out

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under higher H<sub>2</sub> pressure, higher temperature and for longer time [28-31]. Carbon nanotube supported nickel catalyst was developed by Xiong et al. [33], which gave 92.04% selectivity to 1,5-diaminonaphthalene and 100% conversion of 1,5-dinitronaphthalene under mild conditions, nevertheless the leaching of monometallic Ni catalyst will lead to poor reusability. Moreover, large loading amount of nickel will result in agglomeration and sintering, which will bring bad effects on catalyst activity and reusability. Active metals doped with other metal promoter to obtain non-noble bimetallic catalysts have been extensively studied, which present high stability, activity and selectivity in comparison with monometallic catalysts for its better particle dispersion and synergistic catalytic effects among different metals [34-49]. Liu et al. [41] found that doping Cu in Ni-based catalyst will decrease Ni particle size and promote its dispersion, and thus enhance the alkynes hydrogenation activity, and the selectivity to ethene increases because of the electron transfer from Cu to Ni and thus favors ethene species desorption. Lv et al. [42] reported that the addition of copper in MgO-Cu-Ni/MWCNT can lead to better nickel nanoparticles dispersion, larger metallic surface area and facilitate the reduction of nickel oxide at lower temperature, hence improve the catalytic performance for adiponitrile hydrogenation under mild conditions. In addition, Shen and Chen [43] showed that addition of Co in NiB decreased the particle size and improved the stability of NiCoB nanoalloy catalysts in p-chloronitrobenzene hydrogenation. Several studies [44-47] also showed that introduction of Co in Ni-based catalyst decreased the particle size and reduced the reduction temperature of NiO species. The most efficient Ni-Fe bimetallic catalyst for guaiacol hydrodeoxygenation was reported by Fang et al. [48]. It showed that incorporation of Fe in Ni/CNT formed Ni-Fe alloys, reduced the crystallite size and inhibited the sintering of metal nanoparticles. Moreover, ZnO has also been used as the promoter in Ni/ZnO/Al<sub>2</sub>O<sub>3</sub> in partial hydrogenation of Sunflower oil [49] and it was found that ZnO acted as the spacer in Ni crystallites to impede the sintering of Ni particles, leading to higher Ni surface area and better dispersion. Thus, it is worth to develop nonnoble Ni-based bimetallic catalysts with high dispersion and combined catalytic effects.

Activated carbon is widely used as support to load active metals because of its chemical stability, tailored pore size distribution, high specific surface area and capacity to be functionalized [50]. In this work, bimetallic Ni-M/AC (M = Cu, Co, Fe or Zn) catalysts were prepared by incipient wetness impregnation method and applied in 1-ni-tronaphthalene hydrogenation, among all the catalysts studied, the Ni-Zn/AC-350 shows the best catalytic performance under very mild conditions. Such activated carbon supported nickel-based bimetallic catalysts with lower cost are expected to replace the present noble metal catalysts in industry.

# 2. Experimental

# 2.1. Materials

The activated carbon with specific surface area range from 1200-1400 m<sup>2</sup> g<sup>-1</sup> were bought from Fujian Xinsen carbon Co., Ltd. Aromatic nitro compounds was obtained from Beijing Bailingwei Co., Ltd. Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), Iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), Cobalt nitrate (Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 5% Pd/C with 40–60 % H<sub>2</sub>O were bought from Shanghai Aibi Chemistry Reagent Co., Ltd. The aromatic amine (99 wt. %) standard sample was purchased from Beijing Bailingwei Co., Ltd.

### 2.2. Catalyst preparation

Ni-base bimetallic catalysts were prepared by impregnation method. To prepare the Ni-Zn/AC, 1.5 g activated carbon was impregnated in 5 mL of aqueous solution including 0.75 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.069 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, the slurry was treated under ultrasonic for

0.5 h and impregnated for 12 h, followed by drying at 110°C for 12 h. Finally, the obtained solids were calcined at 350°C for 4 h under nitrogen and reduced under hydrogen at 350°C for 2 h. In addition, in order to study the effect of reduction temperature on catalytic performance, the bimetallic Ni-Zn/AC catalyst and monometallic Ni/AC catalyst were reduced at different temperature and the catalysts were marked as Ni-Zn/AC-T and Ni/AC-T (T = 300°C, 350°C, 400°C).

# 2.3. Catalytic reaction

The liquid phase hydrogenation of 1-nitronaphthalene was carried out in a 50 mL Teflon-lined stainless-steel autoclave reactor with 0.1 g catalyst, 2 g 1-nitronaphthalene and 20 mL *N*,*N*-dimethylformamide (DMF), then the reaction was conducted at 80°C and 0.6 MPa H<sub>2</sub> pressure under 400 rpm for 5 h. After the reaction, the catalysts were separated by filtration. The reactant and the product were analyzed by high performance liquid chromatography method. Additionally, the catalysts were filtered from the reaction solution and used for the next run without any other treatment to test the reusability.

### 2.4. Catalysts characterizations

The Powder X-ray diffraction (XRD) measurements were carried out using a Japan Rigaku D/Max 2550 VB<sup>+</sup> 18 kw X-ray diffract meter with Cu K $\alpha$  radiation operating at 40 kV and 30 mA, with a scanning speed of 10° min<sup>-1</sup> in the range of 2 $\theta$  = 10-90°.

Nitrogen adsorption-desorption was performed on a NOVA-2200e automated gas sorption system to measure the specific surface area, pore size distribution and pore volume of the samples. Specific surface area was determined by Brunauer-Emmett-Teller (BET) method, pore size distribution and pore volume were evaluated from the desorption isotherm branch using the Barrette-Joyner-Halenda (BJH) method.

Fourier transform infrared (FT-IR) spectra of the activated carbon was recorded on a Nicolet 380 spectrometer.

The quantitative elemental analysis of active metals was determined by IRIS 1000 ICP-AES (Thermo Elemental, USA).

The hydrogen chemisorption of the samples were examined on Micromeritics 2920. Before starting the hydrogen chemisorption procedure, the samples were reduced in a stream of  $10\% H_2/Ar$ , and then Ar stream was used to remove the adsorbed hydrogen on the nickel surface. The samples were then cooled down to room temperature under Ar stream, and injected with hydrogen pulses until the eluted areas of consecutive pulses became constant. The stoichiometric adsorption of hydrogen was assumed to calculate the amount of nickel atoms, and nickel surface area was calculated from the nickel atomic cross section area.

The X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al-K $\alpha$  radiation, and operated at a invariable transmission energy pass (80 eV). The peak corresponding to carbon 1 s (at 284.6 eV with an accuracy of  $\pm$  0.05 eV) was taken to refer to correct binding energy (BE) values of different elements in the samples.

The temperature programmed H<sub>2</sub> reduction (TPR) profiles of the samples were obtained from ChemBET-3000 equipped with a TCD detector to monitor the H<sub>2</sub> consumption. For each TPR measurement, 60 mg of sample was placed in a quartz tube, heated to 200°C with the rate of 10°C/min under 100 mL/min Ar for 120 min. The sample was then cooled down to 70°C and then heated from 70°C to 700°C at the rate of 10°C/min under a stream of 10% H<sub>2</sub>/Ar at the speed of 100 mL/min.

Transmission electron microscopy (TEM) was carried on a Jem2100 F electron microscope with an accelerating voltage of 200 kV. Before starting the TEM characterization, the powder samples were treated under ultrasonic in anhydrous ethanol, and then dripped on copper grids covered with a porous carbon film. The different elements mapping of the samples were conducted under STEM mode with the



Fig. 1. FT-IR spectra of activated carbon.

EDX detector as recorder.

# 3. Results and discussion

### 3.1. Characterization of catalyst

### 3.1.1. FT-IR

Fig. 1 presents the FT-IR spectra of the activated carbon. The peaks of  $3450 \text{ cm}^{-1}$  and  $1633 \text{ cm}^{-1}$  are attributed to the tensile and flexural vibration of O–H bond in water, and the peaks of  $1400 \text{ cm}^{-1}$  and  $1070 \text{ cm}^{-1}$  are attributed to the existence of the carboxylic acids [33]. It indicates that the activated carbon support contains a small amount of oxygen-containing species, which could improve the dispersibility of activated carbon in water and enhance the specific nucleation sites for the anchoring of metal particles [33].

#### 3.1.2. XRD

The samples were calcined at 350°C for 4 h under nitrogen and reduced at 350°C for 2 h under hydrogen before XRD characterization. Fig. 2 shows XRD patterns of Ni/AC with different Ni loading amount. The peak at  $2\theta = 23^{\circ}$  is corresponded to carbon [51], the peaks at  $2\theta = 44^{\circ}$ , 52°, and 77° (JCPDS #04-0850) are ascribed to (111), (200), and (220) lattice planes of the metal Ni and the peak of 37.2° and 62.5° (JCPDS #47-1049) are indexed to NiO (111) and NiO (220). However, no obvious diffraction peaks of NiO species are observed in 3 wt % Ni/AC and 5 wt % Ni/AC, probably due to high dispersion when Ni loading is low. And the characteristic diffraction peak of nickel becomes sharp with the increment of Ni loading amount, which indicates that larger nickel particle size is obtained.

The XRD patterns of the reduced Ni-based bimetallic catalysts with 10 wt % Ni and 1 wt % promoter metal M (M = Cu, Co, Fe or Zn) are shown in Fig. 3. As we can see, diffraction peak at  $2\theta = 23^{\circ}$  for all the samples is correspond to carbon [51], the significant diffraction peaks observed at  $2\theta = 44^{\circ}$ , 52°, and 77° (JCPDS #04-0850) are ascribed to (111), (200), and (220) lattice planes of the metal Ni, respectively, and the diffraction peaks at  $2\theta = 37.2^{\circ}$ , and 62.5° (JCPDS #47-1049) are



Fig. 2. XRD patterns of (a) 15% Ni/AC, (b) 10% Ni/AC, (c) 5% Ni/AC, (d) 3% Ni/AC.



Fig. 3. XRD patterns of (a) Ni-Zn/AC, (b) Ni-Fe/AC, (c) Ni-Co/AC, (d) Ni-Cu/AC, (e) Ni/AC.

attributed to (111), (220) reflections of the NiO phase. No obvious diffraction peaks of promoter metal species are observed, probably due to the lower amount and better dispersion. It must be noted that the peaks of metal Ni in bimetallic catalysts were much broader than that of monometallic nickel catalysts, indicating that promoter metal M (M = Cu, Co, Fe or Zn) can effectively inhibit nickel sintering and form smaller nickel crystallite with better dispersion on the catalyst surface [42,47,48,52]. And it can be seen from Table 1 that the average Ni crystallite sizes are listed in the following order: Ni-Cu > Ni-Co > Ni-Fe > Ni-Zn.

The effects of reduction temperature on the property of bimetallic Ni-Zn/AC and monometallic Ni/AC are investigated. The XRD diffraction patterns of the samples are displayed in Fig. 4. It can be seen that the samples reduced at 300°C show five characteristic diffraction peaks at  $2\theta = 23^{\circ}$ , 37.2°, 44°, 62.5°, and 77°, the samples reduced at 350°C display six distinct diffraction peaks at  $2\theta = 23^{\circ}$ , 37.2°, 44°, 62.5°, and 77°, the samples reduced at 350°C display six distinct diffraction peaks at  $2\theta = 23^{\circ}$ , 37.2°, 44°, 52°, 62.5°, and 77°, the samples reduced at 400°C reveal four obvious diffraction peaks at  $2\theta = 23^{\circ}$ , 44°, 52° and 77°. As we can see, metal Ni nanoparticles are formed even at relatively low temperature of 300°C, the diffraction peak of metal Ni becomes strong and the crystallinity is improved with the increment of reduction temperature, meanwhile the nickel particle size increases, and more NiO species are reduced when the reduction temperature increases to 400°C.

# 3.1.3. $N_2$ adsorption-desorption

The N<sub>2</sub> adsorption/desorption isotherm and BJH pore size distribution patterns of the samples are shown in Fig. 5, it presents type IV adsorption isotherm, which indicates that the samples have micropore and mesoporore structure [53,54]. The specific surface area, average pore diameter and pore volume of the samples are summarized in Table 1. N<sub>2</sub> adsorption/desorption data indicates that the activated carbon support has the specific surface area of  $1438.3 \text{ m}^2 \text{ g}^{-1}$ , pore volume of  $0.18 \text{ cm}^3 \text{ g}^{-1}$  and pore size of 2.8 nm. After adding 10 wt% Ni and 1 wt% promoter metal M (M = Cu, Co, Fe or Zn) to activated carbon, the specific surface area and pore volume of the samples decrease probably due to the presence of small metal particles in the pore of activated carbon [54], while the pore size remains almost unchanged [55,56].

# 3.1.4. $H_2$ chemisorption

The hydrogen chemisorption data are shown in Table 2. It can be seen that Ni/AC-400 shows the lowest H<sub>2</sub> uptake quantity, the lowest metallic surface area and dispersion. And bimetallic Ni-M/AC-350 (M = Cu, Co, Fe or Zn) catalysts present better results than Ni/AC-350. Some researchers have found that the introduction of promoter metal M (M = Cu, Co, Fe or Zn) helps to enhance the hydrogen uptake quantity and metal dispersion [41,42,47,49,57]. And Ni-Zn/AC-350 exhibits the largest H<sub>2</sub> uptake quantity, metallic surface area and the best nickel

# Table 1 Textural properties of the samples

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Sample	Ni(wt %) <sup>a</sup>	Ν	M <sub>1</sub> <sup>a</sup> (wt %)	$S_{BET}(m^2.g^{-1})$	$V_{pore}(cm^3.g^{-1})$	D <sub>pore</sub> (nm)	D <sub>Ni</sub> (nm) <sup>b</sup>	D <sub>Ni</sub> (nm) <sup>c</sup>
AC	-	_		1438.3	0.18	2.8	-	_
Ni/AC	9.95	-		1198.8	0.14	2.8	8.3	7.2
Ni-Cu/AC	10.10	1.02		1190.2	0.13	2.7	7.2	6.5
Ni -Co/AC	9.92	0.96		1199.4	0.13	2.8	6.8	5.9
Ni -Fe/AC	10.00	1.01		1095.5	0.11	2.8	6.3	5.3
Ni -Zn/AC	10.03	0.92		1186.7	0.12	2.7	5.7	4.6

M1: promoter metal (Cu, Co, Fe or Zn), a: Determined with ICP-AES, b: Calculated from XRD, c: Calculated by TEM images.



Fig. 4. XRD patterns of (a) Ni/AC-400, (b) Ni-Zn/AC-400, (c) Ni/AC-350, (d) Ni-Zn/AC-350, (e) Ni/AC-300, (f) Ni-Zn/AC-300.

dispersion, which might favor the hydrogenation process of aromatic nitro compounds.

# 3.1.5. H2-TPR

Fig. 6 shows the H<sub>2</sub>-TPR characterization patterns of the samples calcined at 350°C for 4 h under flowing nitrogen. It can be seen that all the samples possess two broad hydrogen consumption peaks, the one is located at lower temperature of 650–700 K, which is attributed to the reduction of nickel oxide, the other around 750–850 K is corresponded to the reduction of amorphous C species in the presence of nickel [58,59]. Bian et al. reported that nickel can promote the methanation of carbon nanotubes when the temperature surpassed 773 K [60]. Compared with monometallic catalyst precursor NiO/AC, the bimetallic catalysts make the reduction peaks of nickel oxide shift toward lower temperature, indicating that promoter metals (M = Cu, Co, Fe or Zn) aid in NiO reduction. The reason may be that the synergic effect between nickel and promoter metals (M = Cu, Co, Fe or Zn) will decrease the reduction activation energy of NiO [34,41,50,54,55].

**Table 2** H<sub>2</sub> chemisorption data of the samples.

Catalyst	H <sub>2</sub> chemisorption data					
	$H_2$ uptake quantity ( $\mu$ Lg <sup>-1</sup> )	Metallic surface areas $(m^2 g^{-1})$	Metal dispersion (%)			
Ni/AC-350	95.32	2.31	4.40			
Ni/AC-400	54.72	1.76	2.85			
Ni-Cu/AC-350	133.74	2.52	6.01			
Ni-Co/AC-350	139.32	2.61	7.34			
Ni-Fe/AC-350	147.21	2.83	7.65			
Ni-Zn/AC-350	163.45	3.12	8.05			
Ni-Zn /AC-400	81.74	2.01	4.23			



Fig. 6.  $H_2$ -TPR profiles of (a) 10% Ni/AC, (b) Ni-Cu/AC, (c) Ni-Co/AC, (d) Ni-Fe/AC, (e) Ni-Zn/AC.

#### 3.1.6. XPS

Fig. 7 exhibits the Ni  $2p_{3/2}$  spectra of the samples. The peaks in Ni  $2p_{3/2}$  XPS spectra are located at the BE of 852.8 eV to 853.1 eV, 854.8 eV to 855.1 eV, and 856.4 eV to 856.7 eV, which are attributed to Ni°, Ni<sup>2+</sup>, and Ni<sup>3+</sup>, respectively [48]. Additionally, the shake-up



Fig. 5. N2 adsorption-desorption isotherm and BJH pore size distribution of (a) AC, (b) Ni/AC, (c) Ni-Cu/AC, (d) Ni-Co/AC, (e) Ni-Fe/AC, (f) Ni-Zn/AC.



Fig. 7. XPS patterns of (a) Ni/AC, (b) Ni-Cu/AC, (c) Ni-Co/AC, (d) Ni-Fe/AC, (e) Ni-Zn/AC.

Table 3

Surface composition of samples.

Catalyst	XPS Peak area ratio (%)			
	Ni°	Ni <sup>2+</sup>	Ni <sup>3+</sup>	
Ni/AC	20.3	37.5	42.2	
Ni-Cu/AC	22.1	40.5	37.4	
Ni-Co/AC	23.4	39.6	37.0	
Ni-Fe/AC	24.5	38.8	36.7	
Ni-Zn/AC	27.5	37.4	35.1	

satellites peak appears at 861.3 eV, which is accompanied by multiple division of binding energy of the oxidized nickel [61]. Compared with monometallic catalyst, the intensity of Ni° increases with the introduction of promoter metals (Table 3), indicating that the synergic effect between nickel and promoter metals (M = Cu, Co, Fe or Zn) aids in NiO reduction [42,49,62-64]. This is consistent with the result of H<sub>2</sub>-TPR in Fig. 6. Furthermore, compared with Ni/AC, the binding energy of Ni° in Ni-Cu/AC (Fig. 7 b) shifts towards lower binding energy (BE) (-0.3 eV), the reason may be the charge transfer from Cu to the adjacent Ni since stronger electronic interactions take place between copper and nickel species [41,65,66], and it proves that doping of Cu can lead to the formation of Ni-Cu alloy [41,42]. According to the electron-band theory, nickel has free d-orbitals delocalized in the conductivity band, while copper has free d-electrons. The interaction between Ni and Cu will result in the filling of the d-zone of Ni [67]. As for promoter metals (M = Co, Fe or Zn), the results of XPS show that there is no obvious charge transfer to nickel. Typically, Liu et al. reported that the characteristic peak of metallic nickel species in Ni-Cu/MMO shifted towards lower binding energy (BE) (-0.4 eV) in comparison with Ni/MMO [41].

Table 4	
Surface composition of the samples.	

Catalyst	XPS Peak area ratio (%)				
	Ni°	Ni <sup>2+</sup>	Ni <sup>3+</sup>		
Ni/AC-300	10.2	41.2	48.6		
Ni/AC-350	20.3	37.5	42.2		
Ni/AC-400	25.1	39.2	35.7		
Ni-Zn/AC-300	14.5	40.6	44.9		
Ni-Zn /AC-350	27.5	37.4	35.1		
Ni-Zn /AC-400	31.7	35.2	33.1		

In addition, the covalent of Ni in bimetallic Ni-Zn/AC and monometallic Ni/AC under different reduction temperature was characterized by XPS. The Ni  $2p_{3/2}$  spectra of the samples are shown in Fig. 8. The results indicate that a certain proportion of nickel oxides still exist even the reduction temperature increases to 400°C, the content of Ni° in Ni-Zn/AC is greater than that of Ni/AC under the same reduction temperature (Table 4), hence, Ni-Zn/AC presents higher catalytic activity.

## 3.1.7. TEM

Fig. 9 shows the TEM images of the samples. It can be seen from Fig. 9 a that obvious agglomeration exists in Ni/AC, and the mean particle size is about 7.1 nm. As for promoter metal doped Ni-based catalysts Ni-M/AC (M = Cu, Co, Fe or Zn) in Fig. 9 b, c, d and e, the doped metal can prevent nickel sintering in a certain degree [50,68,62], thus smaller Ni nanoparticles with mean particle sizes of 6.5 nm, 5.9 nm, 5.3 nm and 4.6 nm disperse uniformly on the surface of the support, this is in agreement with the XRD results. In addition, uniform dispersion of metallic particles is beneficial to the exposure of catalytic active sites, hence improves catalytic performance [69].

Fig. 9 a, e and Fig. 10 a, b presents TEM images of Ni-Zn/AC and Ni/ AC reduced under 350°C and 400°C. It was observed that Ni-Zn/AC and Ni/AC reduced at 350°C show highly dispersed metal particles with an average size of 4–7 nm. However, relatively larger particles with an average size of 7–9.5 nm were observed when the reduction temperature increases to 400°C, the particles sintering and agglomeration may occur under higher temperature. In addition, compared with Ni/AC, Ni-Zn/AC shows well dispersion under the same reduction temperature, which further prove that introduction of promoter metal Zn favors Ni particles dispersion.

Ni-Zn/AC-350 was characterized by using high-resolution transmission electro microscope (HRTEM), scanning transmission electro microscope-energy dispersive X-ray (STEM-EDX) and elemental mapping. Meanwhile, the crystal lattice of Ni-Cu alloy in Ni-Cu/AC-350 was measured by HRTEM. It presents that the lattice distance of 0.205 nm (Fig. 11 a) is assigned to (111) plane spacing of Ni-Cu alloy [42]. It can be seen from Fig. 11 b that there exists the lattice distance of 0.204 nm, which is ascribed to (111) plane spacing of Ni (JCPDS #04-0850), and



Fig. 8. XPS patterns of (a) Ni/AC-300, (b) Ni/AC-350, (c) Ni/AC-400, (a1) Ni-Zn/AC-300, (b1) Ni-Zn/AC-350, (c1) Ni-Zn/AC-400.



Fig. 9. TEM pictures (a) Ni/AC, (b) Ni-Cu/AC, (c) Ni-Co/AC, (d) Ni-Fe/AC, (e) Ni-Zn/AC.

the lattice distance of 0.190 nm is assigned to (102) plane spacing of ZnO (JCPDS #36-1451). The small amount of ZnO served as the spacer between Ni crystallites is to prevent the formation of bulky Ni particles. Similarly, Wong et al. found that bimetallic Ni/ZnO/Al<sub>2</sub>O<sub>3</sub> presented less sintering and better dispersion than that of monometallic Ni/Al<sub>2</sub>O<sub>3</sub> because ZnO acts as the physical spacer between Ni crystallites [49]. The elemental mapping analysis based on EDS indicates that nickel and zinc are dispersed homogeneously on the activated carbon support (Fig. 11 e, f).

#### 3.2. Catalytic performance

The prepared catalysts were applied in 1-nitronaphthalene hydrogenation and the results are shown in Fig. 12. The main intermediates include hydroxynaphthalene and hydrazonaphthalene, while the main product is 1-naphthylamine. Other intermediates such as nitrosonaphthalene (NSN), N-naphthylhydroxylamine (HN), azoxynaphthalene (AON), azonaphthalene (AN) and hydrazonaphthalene (HAN) will appear in this reaction (Scheme 1). In "routel", the rate of HN hydrogenation to 1-naphthylamine is relatively slow, hence the NSN and HN is accumulated during this process [70]. Therefore, in "routeII", NSN reacts with HN to form AON, and AON can be reduced to AN, and then AN can be hydrogenated to HAN and finally to 1-naphthylamine.

Since the reaction takes place on the surface of the catalyst, it follows the classical Langmuir–Hinshelwood model [71]. Hydrogen molecules and 1-nitronaphthalene can be adsorbed onto the surface of the bimetallic nanoparticles, and both of the adsorptions are reversible. Under the catalysis of the bimetallic nanoparticles, the hydrogen molecules may dissociate, then active surface hydrogen species are thus



Fig. 10. TEM pictures (a) Ni/AC-400, (b) Ni-Zn/AC-400.



Fig. 11. (a) HRTEM of Ni-Cu/AC, (b) HRTEM of Ni-Zn/AC, (c) HAADF-STEM image of Ni-Zn/AC, (d-f) the corresponding elemental mappings of Ni-Zn/AC.



Fig. 12. Catalytic performance; Reaction conditions:1-nitronaphthalene, 2 g; DMF, 20 mL; Catalyst, 0.1 g; Temperature, 80°C; H2 pressure, 0.6 MPa; Time, 5 h, a 4 h.



Scheme 1. The possible reaction routes of the 1-nitronaphthalene hydrogenation.

generated and bonded to the surfaces of the bimetallic nanoparticles. The adsorbed 1-nitronaphthalene can be reduced to 1-naphthylamine by these active hydrogen species derived from the hydrogen molecules. Because of the much weaker adsorb ability of the amino groups than that of the nitro groups, 1-naphthylamine may desorb readily from the catalyst surface once generated [72]. So the reaction is proceed spontaneously.

It can be seen from Fig. 12 a that AC without active metal does not show catalytic activity in 1-nitronaphthalene hydrogenation, while high cost noble metal catalyst 5% Pd/C shows 100% 1-nitronaphthalene conversion and 98.48% selectivity to 1-naphthylamine under 80°C, 0.6 MPa H<sub>2</sub> pressure and 4 h. The unreduced 10% NiO/AC and 1% M/AC (M = Cu, Co, Fe or Zn) reduced under 350°C are also tested in 1-nitronaphthalene hydrogenation, but these catalysts do not show catalytic activity. For Ni/AC catalyst, as the Ni loading amount increases from 3% to 15%, 1-nitronaphthalene conversion increases from 30.50% to 88.03% and the selectivity to 1-naphthylamine increases from 79.00% to 88.21%. The conversion of 1-nitronaphthalene and the selectivity to 1-naphthylamine present unconspicuous increases with the increment of the Ni loading amount from 10 wt % to 15 wt %, therefore 10% Ni loading amount was adopted.

In order to cut catalyst cost, non-noble bimetallic Ni-M/AC (M = Cu, Co, Fe or Zn) catalysts are prepared and tried in 1-nitronaphthalene hydrogenation, and the results are shown in Fig. 12 b. Notably, in the case of monometallic 10% Ni/AC, 77.05% conversion of 1-nitronaphthalene and 87.03% selectivity to 1-naphthylamine are obtained. However, in bimetallic Ni-M/AC (M = Cu, Co, Fe or Zn) catalysts, the catalytic activity is greatly improved and Ni-Zn/AC gives 92.20% 1-nitronaphthalene conversion under the same reaction conditions. The reason may be the strong interaction between promoter metals and nickel, H<sub>2</sub>-TPR in Fig. 6 shows that the promoter metals can enhance the nickel oxide reduction. What is more, it can be seen from XPS in Fig. 7 that the promoter metals can promote much more Ni° exposure on the surface of the support, moreover, it can be seen from XRD in Fig. 3 and TEM in Fig. 9 that the promoter metals can inhibit nickel nanoparticles agglomeration so as to obtain smaller nickel particles and improve its dispersion. The selectivity to 1-naphthylamine is more than 90% over Ni-Co/AC, Ni-Fe/AC and Ni-Zn/AC, which indicates that deoxygenation of HN to 1-naphthylamine is prone to take place on smaller nickel particles [73,74]. However, bimetallic Ni-Cu/ AC gives only 80.12% selectivity to 1-naphthylamine, the reason may be the transfer of charge from Cu to the adjacent Ni, which results in disadvantage of electron-rich nickel to the adsorption of N-naphthylhydroxylamine, and thus prevent further hydrogenation of N-naphthylhydroxylamine to 1-naphthylamine. Similarly, Chen et al. found that the interfacial electronic effects can control the reaction selectivity in nitrobenzene hydrogenation over platinum catalysts, furthermore, high selectivity to N-hydroxylaniline was obtained by adjusting the surface electron of platinum nanowires with ethylenediamine, and the adsorption of electron-deficient nitrobenzene was favoured by electronrich Pt, thus preventing further hydrogenation of N-hydroxylaniline to aniline [75].

The reduction temperature has great influence on the microstructure and surface composition of the catalyst, hence affects the catalytic performance [33,35]. Too low or too high reduction temperature is not good for either monometallic Ni/AC or bimetallic Ni-Zn/ AC catalyst, lower content of Ni° is obtained under relatively lower reduction temperature of 300°C, while it appears Ni sintering and agglomeration when the reduction temperature increases to 400°C (Fig. 12 c). 1-nitronaphthalene hydrogenation occurs on the surface of the active metal nanoparticles, hence the catalyst with good metal dispersion generally presents good catalytic activity. However, high temperature will cause the sintering of nanoparticles, which may result in a decrease in the amount of the exposed Ni°. Although the total Ni° content of Ni-Zn/AC-400 is higher than that of Ni-Zn/AC-350, the amount of effective Ni° involved in the reaction is less than that of Ni-Zn/AC-350. It can be seen from Table 2 that Ni-Zn/AC-350 exhibits better metal dispersion (8.05%) than that of Ni-Zn/AC-400 (4.23%) and the highest H<sub>2</sub> uptake quantity of  $163.45\mu$ Lg<sup>-1</sup>. Hence, Ni-Zn/AC-350 presents better catalytic performance than that of Ni-Zn/AC-400. The similar results are obtained in monometallic Ni/AC. And Ni/AC-350 gives 77.15% conversion of 1-nitronaphthalene and 87.03% selectivity to 1-naphthylamine, while Ni-Zn/AC-350 gives 92.20% conversion of 1-nitronaphthalene and 91.70% selectivity to 1-naphthylamine.

Bimetallic Ni-Zn/AC-350 presented good catalytic performance in 1-nitronaphthalene hydrogenation, it was tried in other aromatic nitro compounds hydrogenation such as 1,5-dinitronaphthalene, 1,8-dinitronaphthalene, nitrobenzene, o-chloronitrobenzene, m-chloronitrobenzene and p-chloronitrobenzene. It can be seen from Table 5 that 95.63% yield of 1,5-diaminonaphthalene, 97.25% yield of 1,8-diaminonaphthalene, 98.36% yield of aniline, 93.57% yield of o-chloroaniline, 93.54% yield of m-chloroaniline and 94.02% yield of p-chloroaniline are obtained under mild conditions.

# 3.3. Influence of the reaction conditions

The effects of reaction temperature on the reaction catalyzed by Ni-Zn/AC-350 at 0.6 MPa  $H_2$  pressure and reaction time of 5 h are shown

Table 5

The hydrogenation of aromatic nitro compounds to corresponding aromatic amine over Ni-Zn/AC-350.

		•				
Reactant	Product	Time(h)	T(°C)	P(Mpa)	Conversion (%)	Yield(%)
1,5-dinitronaphthalene	1,5-diaminonaphthalene	5	110	0.6	100	95.63
1,8-dinitronaphthalene	1,8-diaminonaphthalene	6	110	0.6	100	97.25
Nitrobenzene	Aniline	4	80	1	100	98.36
o-chloronitrobenzene	o-chloroaniline	4	80	1	100	93.57
m-chloronitrobenzene	m-chloroaniline	4	80	1	100	93.54
p-chloronitrobenzene	p-chloroaniline	4	80	1	100	94.02

Reaction conditions: reactant, 2 g, DMF, 20 mL, Catalyst, 0.1 g.





Fig. 14. XRD and TEM patterns of Ni-Zn/AC of after four runs.

in Fig. 13 a. The conversion of 1-nitronaphthalene and the selectivity to 1-naphthylamine increases with the increment of reaction temperature from 70 to 90°C, it gives 100% 1-nitronaphthalene conversion and the selectivity to 1-naphthylamine is up to 96.82% under 90°C.

Fig. 13 b indicates the effects of hydrogen pressure on the reaction



Fig. 13. Influence of the reaction conditions and reusability of catalyst; (a) Reaction conditions:1-nitronaphthalene, 2g; DMF, 20 mL; Catalyst, 0.1 g; H<sub>2</sub> pressure, 0.6 MPa; Time, 5 h; (b) Reaction conditions:1-nitronaphthalene, 2 g; DMF, 20 mL; Catalyst, 0.1 g; Temperature, 90°C; Time, 5 h; (c) Reaction conditions:1-nitronaphthalene, 2 g; DMF, 20 mL; Catalyst, 0.1 g; Temperature, 90°C; H<sub>2</sub> pressure, 0.6 MPa; (d) Reaction conditions:1-nitronaphthalene, 2 g; DMF, 20 mL; Catalyst, 0.1 g; Temperature, 90°C; H<sub>2</sub> pressure, 0.6 MPa;Time, 5 h.

catalyzed by Ni-Zn/AC-350 under 90°C and reaction time of 5 h. It can be seen that the conversion of 1-nitronaphthalene reaches to 100% and selectivity to 1-naphthylamine is up to 96.82% when H<sub>2</sub> pressure increases to 0.6 MPa.

Fig. 13 c presents the effects of reaction time on the reaction catalyzed by Ni-Zn/AC-350 under 90°C and 0.6 MPa H<sub>2</sub> pressure. It can be seen that 1-nitronaphthalene cannot be totally converted when the reaction time is less than 5 h. As the reaction time increases to 5 h, 1nitronaphthalene conversion increases to 100% and the selectivity to 1naphthylamine is up to 96.82%. In a word, bimetallic Ni-Zn/AC-350 gives the best catalytic performance under mild conditions of 90°C, 0.6 MPa H<sub>2</sub> pressure and 5 h.

# 3.4. The reusability of catalyst

The recycle of the bimetallic Ni-Zn/AC-350 is carried out by using the filtrated catalyst without other treatment for the next run. It can be seen from Fig. 13 d that the catalytic performance remains almost unchanged for the second run, but the yield of 1-naphthylamine decreases a little for the third and the fourth run, which is attributed to the leaching of the Ni on the surface proved by the ICP-AES analysis of the nickel loading amount of the recycled catalyst, it decreases from 10% to 9% after the fourth run and ICP-AES analysis shows that 0.95% nickel is leaked to the reaction solution. In addition, the XRD and TEM characterization results of the catalyst after the fourth run show that the

Fig. 15. XPS patterns of Ni-Zn/AC of after four runs.

diffraction peaks of metallic nickel become more sharper and the nickel nanoparticles tend to agglomerate (Fig. 14), as for the XPS characterization results, it shows that the oxidation state of nickel has little change after the fourth run (Fig. 15).

## 4. Conclusion

In conclusion, a series of highly dispersed bimetallic Ni-M/AC (M = Cu, Co, Fe or Zn) catalysts were prepared by incipient wetness impregnation method and applied in 1-nitronaphthalene hydrogenation to 1-naphthylamine under mild reaction conditions. The prepared catalvsts were characterized by XRD, BET, H2-TPR, TEM, HRTEM, HAADF-STEM, XPS, ICP, FT-IR and H<sub>2</sub> chemisorption. The results show that introduction of the metal promoter inhibits the sintering of the nickel and enhances the reducibility of the catalysts, leading to higher ratio of effective Ni° on the surface of the support, especially for Ni-Zn/AC-350. The results of XPS indicate that the electron donating effect of Cu promoter increases surface electronic density of Ni, which favors Nnaphthylhydroxylamine desorption, thus impedes its further hydrogenation to 1-naphthylamine. Ni-Zn/AC-350 presents the best catalytic performance in 1-nitronaphthalene hydrogenation to 1-naphthylamine under mild reaction conditions, it gives 100% conversion of 1-nitronaphthalene and 96.82% selectivity to 1-naphthylamine under 0.6 MPa and 90°C for 5 h. Furthermore, it also shows good catalytic performance in hydrogenation reaction of nitrobenzene, chloronitrobenzene, 1,5-dinitronaphthalene and 1,8-dinitronaphthalene.

In summary, with good hydrogenation activity the activated carbon supported Ni doped with Zn promoter catalyst shows, the application prospect in industrial production of aromatic amine from aromatic nitro compounds has been becoming more and more extension.

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