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Hydrogenation of 3-nitro-4-methoxy-acetylaniline with H₂ to

3-amino-4-methoxy-acetylaniline catalyzed by bimetallic copper/nickel

nanoparticles

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ABSTRACT

Monometallic Cu, monometallic Ni, and bimetallic Cu_xNi_y nanoparticles were prepared by a wetness chemical reduction method. Cu-Ni alloy phase was formed in the bimetallic Cu_xNi_y nanoparticles. The bimetallic Cu_xNi_y nanoparticles exhibited higher catalytic activity for the hydrogenation of 3-nitro-4-methoxy-acetylaniline (NMA) with H₂ to 3-amino-4-methoxy-acetylaniline (AMA) than the sole Ni nanoparticles, which was ascribed to the effect of Cu-Ni alloy phase. When the reaction was catalyzed over the bimetallic Cu_{0.7}Ni_{0.3} catalyst at 140 °C for 2 h, the AMA selectivity was 99.4% at the NMA conversion of 95.7%. The reaction activation energy for NMA hydrogenation was 19.74 kJ/mol.

Keywords: 3-Nitro-4-methoxy-acetylaniline; 3-Amino-4-methoxy-acetylaniline; Bimetallic Cu_xNi_y nanoparticles; Hydrogenation; Kinetics

Introduction

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Anilines are valuable chemicals in the production of pharmaceuticals, agricultural chemicals, dyes, polymers, photographic and rubber materials, and chelating agents. ^{1–3} 3-Amino-4-methoxy-acetylaniline (AMA) is one of the most useful anilines in great demand, which is widely used as a coupling component in many commercial dyes because it can give high fastness properties to dyes on hydrophobic fibers and deep shades.⁴ There are two methods for the production of AMA, selective acylation of 2,4-diaminoanisole and reduction of 3-nitro-4-methoxy-acetylaniline (NMA). There are some drawbacks in the acylation process. Byproducts, 4-diacetamidoanisole and 3-amino-6-methoxy-acetanilide, are formed and 2,4-diaminoanisole can be easily oxidized, giving a low selectivity of AMA. Considering that NMA is commercially available at a lower price, reduction of NMA is taken as a favorable process for AMA production, in which the key point is the selection of effective reductant and catalyst.

Iron powder was used as a cheap reductant for the reduction of NMA to AMA under acidic condition in industry. However, a large amount of iron-oxide sludge (1.2 kg sludge/kg product) was also produced, which is a heavy pollutant difficult to deal with industrially.^{5–7} Hydrazine hydrate is commonly used as an efficient reductant for the reduction of nitro-compounds at 50–70 °C and atmospheric pressure.^{8–10} The selectivities and yields of products are significantly affected by the concentration of hydrazine hydrate. At a low concentration of hydrazine hydrate, amines are favorably formed. However, the reduction rate is very low. At a high concentration of hydrazine

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hydrate, many by-products are formed, such as diimide, azoxybenzene, and hydrazobenzene.¹¹ Sodium borohydride also exhibits good activity for the reduction of NMA to AMA, catalyzed by copper nanoparticles.¹² However, the prices of hydrazine hydrate and sodium borohydride are very high, which are not suitable for the reduction of NMA to AMA in industrial scale from the perspective of economy.

Catalytic hydrogenation of nitro-compounds using molecular hydrogen as hydrogen source is considered as the most economical and environmental friendly method for the production of corresponding amines. Metallic catalysts, such as nano Ni,¹³⁻¹⁷ Au-Ni,¹⁸ Raney Ni,^{19,20} Pd/C,²⁰ Pt/C,²¹⁻²³ and Ag,²⁴ are reported active for the hydrogenation reaction. There was hardly any by-product formed in this process, giving a very high selectivity of amine. It is noteworthy that all of these researches focused on the catalytic performances of noble metal and nickel catalysts, the catalytic performances of copper-containing catalysts for the hydrogenation of NMA were rarely investigated. It is well-known that metallic copper is a conventionally used catalyst for hydrogenation reactions because of its high activity and stability as well as cheap price.^{25,26} However, the monometallic copper catalysts are not so active as noble metal and nickel catalysts for the hydrogenation of nitro-compound at a lower reaction temperature. The optimal active temperature of monometallic copper catalyst is over 200 °C, which causes energy consumption and side reactions at such high reaction temperature. According to open literatures, Ni-containing Cu/SiO₂ catalyst exhibited good catalytic activity for the selective synthesis of ethanol via hydrogenation of dimethyl oxalate.^{27,28} The catalytic performance of bimetallic Cu-Ni nanoparticles for the hydrogenation of NMA is worth of study.

In our present work, bimetallic Cu_xNi_y nanoparticles were prepared by a wet chemical reduction method in anhydrous ethanol using Tween-80 as the organic modifier. The chemical structures of the bimetallic Cu_xNi_y nanoparticles were analyzed by XRD and HRTEM techniques. The as-prepared bimetallic Cu_xNi_y nanoparticles were used as the catalysts in the catalytic hydrogenation of NMA with H₂ to AMA. The effect of the Cu and Ni contents in Cu_xNi_y nanoparticles and reaction parameters on the catalytic hydrogenation of NMA was investigated in detail. A power function type reaction kinetic model was used to evaluate the reaction kinetics of NMA hydrogenation over the bimetallic $Cu_0_7Ni_{0.3}$ nanoparticle catalyst.

Experimental

Materials

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The chemicals, copper nitrate (Cu(NO₃)₂·3H₂O), nickel acetate (C₄H₆O₄Ni·4H₂O), sodium hydroxide (NaOH), hydrazine hydrate (N₂H₄·H₂O, 85%), polyoxyethylenesorbitan monooleate (Tween-80, C₂₄H₄₄O₆), NMA, AMA, acetic acid, and anhydrous ethanol were of reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. China. Methanol was of chromatographic grade and was purchased from Sinopharm Chemical Reagent Co., Ltd. China. All the chemicals were used as received without further purification.

Preparation of Cu_xNi_y nanoparticles

 Cu_xNi_y nanoparticles (x and y, mole fractions of Cu and Ni) were prepared by the wet chemical reduction method using hydrazine hydrate as the reductant and Tween-80 as

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the organic modifier, respectively. Considering that Tween-80 could effectively control the particle sizes of metallic Ni and Au nanoparticles and induce the morphology evolution of metallic Ag nanoparticles due to the interaction between Tween-80 molecules and metallic crystallites,²⁹⁻³¹ Tween 80 was selected as the organic modifier in our present work to control the particle sizes of CuxNiv nanoparticles. To completely reduce Ni²⁺ to metallic Ni, a strong reductant, hydrazine hydrate, was used. Typically, given amounts of copper nitrate and Tween-80 (0.38 g)were dissolved in anhydrous ethanol with the Cu²⁺ concentration of 0.4 M. Prescribed amount of nickel acetate ethanol solution (0.4 M) was added to the solution. After the mixture was heated to 60 °C, 40 mL of NaOH (1.8 M) ethanol solution was added dropwise into it to adjust the pH value to ca. 10. Then, a hydrazine hydrate ethanol solution (25 mL in 75 mL anhydrous ethanol) was added dropwise into the mixture and the reaction mixture was refluxed for 4 h under mild stirring. After reduction with hydrazine hydrate, the color of the reaction solution changed to black, indicating that Cu^{2+} and Ni^{2+} were reduced to metallic Cu^{0} and Ni^{0} , respectively. The resultant Cu_xNi_y nanoparticles were cooled to room temperature, centrifugated, washed with anhydrous ethanol, and kept in anhydrous ethanol before they were characterized and used as the catalysts for the hydrogenation of NMA. The preparation conditions of the Cu_xNi_y nanoparticles are listed in Table 1. The inductively coupled plasma (ICP) analysis showed that the contents of Cu and Ni in the Cu_xNi_y nanoparticles were close to those calculated according to their precursors (Table 1).

For comparison, sole Cu and Ni nanoparticles were also prepared according to the

Characterization

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The crystal phases of the as-prepared nanoparticle samples were determined by the X-ray powder diffraction (XRD). The XRD spectra of the samples were recorded on a diffractometer (D8 super speed Bruke-AEX Company, Germany) using Cu K α radiation ($\lambda = 1.54056$ Å) with a Ni filter at room temperature, scanning from 20° to 80° (2 θ).

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained on a microscope (JEM-2100) operated at an acceleration voltage of 200 kV to characterize the morphologies and crystal structures of the nanoparticle samples. Specimens for TEM analysis were prepared by placing a drop of ethanol suspension of nanoparticle sample onto a copper grid coated with a layer of amorphous carbon. The data used for the calculation of particle size distribution for each sample were measured from the TEM images by counting at least 100 individual particles. The average metal particle sizes of samples were calculated by a weighted-average method according to the individual particle sizes of the all counted particles. And the results are listed in Table 1.

The Cu and Ni contents of the Cu_xNi_y nanoparticles were analyzed using inductively coupled plasma (ICP) technique (VISTA-MPX).

Catalytic test

Catalytic hydrogenation of NMA with H_2 was performed in a 500 mL capacity stainless steel autoclave equipped with a magnetically driven impeller. The autoclave

was charged with appointed amounts of NMA, methanol, and catalyst. Firstly, the autoclave was purged with N_2 for 10 min to replace the air inside. When the autoclave was heated up to given reaction temperature at a stirring speed of 100 rpm, pure H_2 was pressurized into the autoclave. After raising the pressure to the desired value, the hydrogenation of NMA started at a stirring speed of 400 rpm. After reacting for a certain time period, the autoclave was cooled to ambient temperature and depressurized for product analysis.

The concentrations of products and remained NMA were analyzed on an Agilent HPLC system equipped with a reverse-phase column (Innoval ASB C18, 5 μ m, 4.6 mm × 250 mm) and a UV detector (λ = 254 nm) at 30 °C. A mixture of acetic acid (0.5 wt.%) aqueous solution and methanol of chromatographic grade (v:v = 55:45) was used as a mobile phase at a flow rate of 0.8 mL/min. The concentrations of products and NMA were analyzed by the external standard method.

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	Catalysts	Raw materials (g)			Average	NIMA	Selectivities (%)		
		Cu(NO ₃) ₂ ·3H ₂ O	C ₄ H ₆ O ₄ Ni ·4H ₂ O	Cu/Ni atomic ratios ^a	and size distributions ^b (nm)	Conversions ^c (%)	HAMA	AMA	TOF ^d (h ⁻¹)
	Cu	3.87	0	/	7.3, 4.0–11.2	0	0	0	/
	Cu _{0.9} Ni _{0.1}	3.87	0.44	0.90:0.10	5.3, 3.3-7.5	65.9	3.5	96.5	6.23
	Cu _{0.7} Ni _{0.3}	3.87	1.71	0.72:0.28	4.2, 2.8–6.1	84.5	1.8	98.2	2.62
	Cu _{0.5} Ni _{0.5}	3.87	3.98	0.52:0.48	4.6, 3.3–6.4	82.2	1.5	98.5	1.51
	Cu _{0.3} Ni _{0.7}	1.94	4.65	0.33:0.67	4.8, 3.4–6.7	76.3	0.8	99.2	0.98
	Ni ^e	0	3.98	/	3.8, 2.1–5.1	24.0	0.3	99.7	0.74

Table 1 The catalytic activities of the Cu_xNi_y nanoparticles for the catalytic hydrogenation of NMA with H₂

^a The atomic ratios of Cu to Ni were determined by ICP.

^b The metal particle sizes were determined from TEM images.

^c Reaction conditions: NMA methanol solution, 150 mL, 0.2 mol L^{-1} ; H₂ pressure, 0.8 MPa; reaction temperature, 120 °C; reaction time, 2 h; catalyst loading, 1.0 g; and stirring rate, 400 rpm.

 d TOF = The moles of converted NMA divided by moles of Ni in Cu_xNi_y catalysts and reaction time, assuming that pure Cu nanoparticles had no catalytic activity under our present reaction conditions.

^e The amount of monometallic Ni nanoparticles used in the catalytic reaction was the same as that present in the Cu_{0.7}Ni_{0.3} catalyst.

Results and discussion

XRD analysis

The XRD patterns of the monometallic Cu, monometallic Ni, and bimetallic $Cu_x Ni_y$ nanoparticles are shown in Fig. 1. The XRD pattern of the monometallic Cu nanoparticle sample showed three diffraction peaks appearing at 20 of 43.3, 50.4, and 74.1°, which are the characteristic peaks corresponding to the (111), (200), and (220) planes of the face-centered-cubic (fcc) copper (JCPDS 04-0836), respectively. For the monometallic Ni nanoparticle sample, three peaks appearing at 20 of 44.5, 51.8, and 76.4° corresponded to the (111), (200), and (220) planes of the face-centered-cubic (fcc) nickel (JCPDS 04-0850), respectively.^{32,33} No impurity diffraction peaks of copper and nickel oxides were detected, indicating that phase-pure monometallic Cu and Ni nanoparticles were prepared under the present experimental conditions. For the bimetallic Cu_{0.9}Ni_{0.1}, Cu_{0.7}Ni_{0.3}, and Cu_{0.5}Ni_{0.5} samples, three diffraction peaks appeared at 20 of 43.4–43.6, 50.5–50.7, and 74.3–74.6°, respectively. These peaks appeared between those of the monometallic Cu and Ni nanoparticles and the 2θ shifted to large value upon increasing the Ni content, revealing that the Cu and Ni components in the bimetallic Cu_{0.9}Ni_{0.1}, Cu_{0.7}Ni_{0.3}, and Cu_{0.5}Ni_{0.5} samples formed Cu-Ni alloy. However, For the $Cu_{0.3}Ni_{0.7}$ sample, in addition to the alloy diffraction peaks, three diffraction peaks appearing at $2\theta = 44.5$, 51.8, 76.4° were indexed as the (111), (200), and (220) planes of metallic Ni. When the mole fraction of Ni was excessive in the bimetallic CuNi sample, in addition to Cu-Ni alloy, metallic Ni nanoparticles were also formed.



Fig.1. XRD patterns of Cu, Ni, and Cu−Ni samples. ●, Cu; ♦, Ni; *, spent catalyst.

TEM and HRTEM analysis

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TEM and HRTEM were used to determine the morphologies, structures, and particle sizes of the monometallic Cu, monometallic Ni, and bimetallic Cu_xNi_y samples. The TEM and HRTEM images are shown in Fig. 2. For the monometallic Cu sample, the TEM image shows that spherical Cu nanoparticles were formed with the average particle size of 7.3 nm and the particle size distribution of 4.0–11.2 nm (Fig. 2a1, Table 1). The lattice fringes of the monometallic Cu nanoparticles were examined to be 0.208 and 0.181 nm, being close to the (111) and (200) lattice spacings of fcc metallic copper, respectively (Fig. 2a2). For the monometallic Ni sample, the spherical Ni nanoparticles were formed with the average particle size distribution of 2.1–5.1 nm (Fig. 2f1). The lattice fringes of monometallic Ni nanoparticles were examined to be 0.203 and 0.176 nm, which are close to the (111) and (200) lattice spacings of fcc metallic Ni nanoparticles were examined to be 0.203 and 0.176 nm, which are close to the (111) and (200) lattice spacings of fcc metallic nickel, respectively (Fig. 2f2).





Fig. 2. TEM and HRTEM images of (a1,a2) Cu, (b1,b2) $Cu_{0.9}Ni_{0.1}$, (c1,c2) $Cu_{0.7}Ni_{0.3}$, (d1,d2) $Cu_{0.5}Ni_{0.5}$, (e1,e2) $Cu_{0.3}Ni_{0.7}$ and (f1,f2) Ni samples.

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The TEM images (Figs. 2b1-e1) of the bimetallic Cu_{0.9}Ni_{0.1}, Cu_{0.7}Ni_{0.3}, Cu_{0.5}Ni_{0.5}, and Cu_{0.3}Ni_{0.7} samples show that the as-prepared bimetallic nanoparticles had the small average particle sizes of 4.2–5.3 nm and the narrow size distributions ranging from 2.8 to 7.5 nm. The HRTEM images of the bimetallic Cu_{0.9}Ni_{0.1}, Cu_{0.7}Ni_{0.3}, and Cu_{0.5}Ni_{0.5} nanoparticles show that the individual nanoparticles were formed by the coalesce of metallic Ni and Cu nanoparticles (Figs. 2b2-d2). The lattice fringes of 0.208–210 nm were close to the (111) lattice spacing of fcc metallic copper while the lattice fringes of 0.202 (or 0.203) and 0.175 (or 0.176) nm were close to the (111) and (200) lattice spacings of fcc metallic nickel, respectively. The HRTEM results certified the formation of Cu-Ni alloy in these bimetallic Cu_xNi_y samples, being in agreement with the results obtained by XRD analysis.

For the $Cu_{0.3}Ni_{0.7}$ sample, in addition to the Cu-Ni alloy nanoparticles, the individual metallic Ni nanoparticles were also detected according to the HRTEM analysis (Fig. 2e2).

Hydrogenation of NMA with H₂ catalyzed by Cu_xNi_y nanoparticles

The catalytic hydrogenation of NMA with H_2 over the bimetallic Cu_xNi_y nanoparticle catalysts was carried out in a methanol solution at 120 °C and 0.8 MPa H_2 for 2 h. The results are listed in Table 1. The monometallic Cu nanoparticles did not exhibit activity for the hydrogenation of NMA. When the monometallic Ni nanoparticles were used to catalyze the hydrogenation of NMA, the conversion of NMA was 24.0% with the selectivity of AMA of 99.7%.

When the bimetallic Cu_{0.9}Ni_{0.1}, Cu_{0.7}Ni_{0.3}, Cu_{0.5}Ni_{0.5}, and Cu_{0.3}Ni_{0.7} nanoparticles

were used to catalyze the hydrogenation of NMA, the bimetallic $Cu_{0.7}Ni_{0.3}$ and $Cu_{0.5}Ni_{0.5}$ catalysts exhibited high catalytic activities for the hydrogenation of NMA, giving the NMA conversions of 84.5% and 82.2%, respectively. When the hydrogenation of NMA was catalyzed by the bimetallic $Cu_{0.7}Ni_{0.3}$ and monometallic Ni catalysts with the same Ni content, the conversion of NMA over the former was more than 3.5 times that over the latter. The results revealed that the formation of Cu-Ni alloy favored the hydrogenation of NMA.

Upon increasing the mole fraction of Ni in the bimetallic catalysts, the selectivities of AMA slightly increased from 96.5% to 99.2% while the selectivities of the intermediate product, 3-hydroxamino-4-methyl-acetylaniline (HAMA) decreased from 3.5% to 0.8%. The monometallic Ni nanoparticles gave the highest selectivity of AMA and the lowest selectivity of HAMA among all the tested catalysts. It could be concluded that high Ni content in the catalyst favored the hydrogenation of HAMA to AMA.

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According to TOF values, it was interesting to find that the TOF values over the bimetallic Cu_xNi_y catalysts were higher than that of the monometallic Ni nanoparticles (0.74 h⁻¹). The bimetallic catalyst with a lower mole fraction of metallic Ni gave higher TOF value. It was reasonable to suggest that the alloying interaction between Cu and Ni in the bimetallic Cu_xNi_y nanoparticles favored the hydrogenation of NMA.

Considering that the $Cu_{0.7}Ni_{0.3}$ catalyst exhibited high catalytic activity for the hydrogenation of NMA to AMA, it was selected as the model catalyst for

investigating the effect of other reaction parameters on the catalytic hydrogenation of

NMA.



Fig. 3. Effect of reaction temperature on the catalytic hydrogenation of NMA over the bimetallic $Cu_{0.7}Ni_{0.3}$ nanoparticles. Reaction conditions: NMA methanol solution, 150 mL, 0.2 mol/L; H₂ pressure, 0.8 MPa; catalyst loading, 1.0 g; and stirring rate, 400 rpm.

Effect of reaction temperature

Fig. 3 shows the conversions of NMA and the selectivities of HAMA and AMA in the hydrogenation of NMA catalyzed by the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst at different reaction temperatures. The NMA conversion and AMA selectivity increased while the HAMA selectivity decreased upon increasing the reaction temperature. After reacting at 140 °C for 2 h, the selectivities of AMA and HAMA were 99.4% and 0.6% at the NMA conversion of 95.7%. The results revealed that a high reaction temperature favored the catalytic hydrogenation of NMA to AMA through HAMA because only HAMA was detected as a byproduct.

Effect of NMA concentration

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The NMA conversions and product selectivities in the hydrogenation of NMA over the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst under different NMA concentrations are shown in Fig. 4. When the reaction was carried out at 140 °C and 0.8 MPa H₂ for 2 h, the conversions of NMA and the selectivities of AMA decreased from 99.1% to 82.7% and from 99.9% to 92.5%, respectively, upon increasing the NMA concentrations from 0.15 to 0.25 mol/L. NMA was efficiently hydrogenated to AMA under the NMA concentration of less than 0.25 mol/L.

Effect of H₂ pressure

When NMA was hydrogenated over the bimetallic Cu_{0.7}Ni_{0.3} catalyst at different H₂

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pressures and 140 °C for 2 h, the NMA conversion and AMA selectivity reached 100% and 99.9%, respectively, upon increasing the H₂ pressure to 1.2 MPa (Fig. 5). High H₂ pressure favored the catalytic hydrogenation of NMA to AMA.



Fig. 4. Effect of NMA concentration on the catalytic hydrogenation of NMA over the bimetallic Cu_{0.7}Ni_{0.3} nanoparticles. Reaction conditions: NMA methanol solution, 150 mL; H₂ pressure, 0.8 MPa; reaction temperature, 140 °C; catalyst loading, 1.0 g; and stirring rate, 400 rpm.



Fig. 5. Effect of H_2 pressure on the catalytic hydrogenation of NMA over the bimetallic Cu_{0.7}Ni_{0.3} nanoparticles. Reaction conditions: NMA methanol solution, 150 mL, 0.2 mol/L; reaction temperature, 140 °C; catalyst loading, 1.0 g; and stirring rate, 400 rpm.



Fig. 6. Effect of catalyst loading on the catalytic hydrogenation of NMA over the bimetallic $Cu_{0.7}Ni_{0.3}$ nanoparticles. Reaction conditions: NMA methanol solution, 150 mL, 0.2 mol/L; H₂ pressure, 0.8 MPa; reaction temperature, 140 °C; and stirring rate, 400 rpm.

Effect of catalyst loading

The conversions of NMA and the selectivities of HAMA and AMA in the hydrogenation of NMA catalyzed by the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst at 140 °C with different catalyst loadings are shown in Fig. 6. When the catalyst loading was 1.4 g, the NMA conversion was 99.9% with the AMA selectivity of 99.6%. The results demonstrated that high catalyst loading favored the conversion of NMA to AMA.

Reaction kinetics

Experimental conditions for kinetic research

A power-function type reaction kinetic equation was used to evaluate the effect of the NMA concentration, H_2 pressure, and reaction temperature on the reaction rate of NMA hydrogenation. The bimetallic $Cu_{0.7}Ni_{0.3}$ nanoparticle catalyst was selected as the model catalyst because it exhibited good catalytic performance for the hydrogenation of NMA.

In order to eliminate the effect of diffusion, the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst with different loadings in the range of 0.6–1.4 g was used for the catalytic hydrogenation of NMA (0.2 mol/L) at 140 °C for 0.5 h. Plotting catalyst loading *vs* NMA conversion gave a straight line (Fig. S1). This result indicated that the initial hydrogenation rate was controlled solely by chemical reaction rather than mass diffusion.^{34,35}

The power-function type reaction kinetic equation for the hydrogenation of NMA is listed as follows.

 $r_0 = -dn_0/(dt \cdot W_{\text{cat}}) = kC_0^{\ a} P_0^{\ b}$ (1)

where k is the rate constant. a and b are the reaction orders with respect to the

concentration of NMA and H₂ pressure. r_0 is the initial reaction rate of NMA, mol/h·g. C_0 is the initial concentration of NMA, mol/L. P_0 is the initial H₂ pressure, MPa. W_{cat} is the catalyst weight, g.

The rate constant k follows the Arrhenius equation Eq. (2).

$$k = A \exp(-Ea/RT) \tag{2}$$

where A is the pre-exponential factor and Ea is the activation energy, kJ/mol. R is the ideal gas constant, 8.314×10^{-3} kJ/mol·K. T is the reaction temperature, K.

In the kinetic experiments, the H_2 pressure is taken constant because the consumed H_2 mount is negligible as compared with the initial H_2 feed at a lower NMA conversion. The initial NMA concentration is used as the value of NMA concentration variable considering that the plot of NMA conversion *vs* reaction time can be taken as a straight line at a lower NMA conversion.

Determination of kinetic parameters

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By taking the natural logarithm of both sides of the Eq. (1), a linear Eq. (3) is obtained as follows.

$$\ln r_0 = \ln(-dn_0/(dt \cdot W_{\text{cat}})) = \ln k + a \ln C_0 + b \ln P_0 \qquad (3)$$

To simulate the reaction orders of *a* and *b* according to Eq. (3), NMA methanol solution with different concentrations was fed into the stainless steel autoclave and then reacted over 1.0 g of $Cu_{0.7}Ni_{0.3}$ nanoparticle catalyst under different H₂ pressures. The conversions of NMA at the reaction temperatures of 100–140 °C are listed in Fig. S2. The initial reaction rates of NMA were calculated at the first 0.5 h.



Fig. 7. Estimation of (a,b) the reaction orders and (c) the reaction activation energy for the power-function type reaction kinetic equation over the bimetallic $Cu_{0.7}Ni_{0.3}$

catalyst.

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Fig. 7a shows the lines by plotting $\ln r_0 vs \ln C_0$ while Fig. 7b shows the lines by plotting $\ln r_0 vs \ln P_0$ at the reaction temperatures ranging from 100 to 140 °C. All the straight lines gave good linear correlations above 0.995. The slopes were close to each other in each figure. The average values of the reaction orders, *a* and *b*, for NMA and H₂ were 0.45 and 1.15, respectively, which were calculated according to the slopes (Table 2).

According to Eq. (3), the rate constants (k) at different reaction temperatures were calculated by using the obtained values of the reaction orders, a and b.

A linear Eq. (4) is obtained by taking the natural logarithm of both sides of the Eq. (2).

 $\ln k = \ln A - (Ea/R)(1/T) \tag{4}$

By plotting $\ln k vs 1/T$, a straight line with the correlation coefficient of 0.9936 was obtained (Fig. 7c). The reaction activation energy (*Ea*) of 19.74 kJ mol⁻¹ and pre-exponential factor (*A*) of 13.59 were calculated according to the slope and intercept of the straight line (Table 2).

Riffettes								
Reaction	Reaction orders					E	Pre-exponential	
temperatures	_	Average	erage b	Average	ln k	$/kJ \cdot mol^{-1}$	factor	
T /ºC	а	а		b			А	
100	0.45		1.16		-3.77103			
120	0.45	0.45	1.15	1.15	-3.40485	19.74	13.59	
140	0.44	4	1.13		-3.15587			

Table 2 Reaction orders, activation energy, and pre-exponential factor of the reaction kinetics

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The reaction kinetic equation for the catalytic hydrogenation of NMA over the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst was written as follows.

$$r_0 = -dn_0/(dt \cdot W_{\text{cat}}) = 13.59 \exp(-19.74/RT)C_0^{0.45} P_0^{1.15} \text{ mol/h}\cdot\text{g}$$
 (5)

Catalyst recycling performance

The recycling performance of the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst for the catalytic hydrogenation of NMA was also investigated and the results are shown in Fig. 8. After reacting at 140 °C for 2 h, the used catalyst was centrifugated and washed with anhydrous ethanol before next recycling. The XRD pattern of the spent catalyst was the same as that of the fresh one (Fig. 1). The conversion of NMA and the selectivity of AMA over the fresh $Cu_{0.7}Ni_{0.3}$ nanoparticles were 95.7% and 99.4%, respectively. After recycling for 4 times, the NMA conversion and AMA selectivity slightly decreased to 93.5% and 96.8%, respectively. It is clear that the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst exhibited excellent recycling performance and stability for the catalytic hydrogenation of NMA to AMA.



Fig. 8. Recycling performance of the bimetallic $Cu_{0.7}Ni_{0.3}$ catalyst for the catalytic hydrogenation of NMA. Reaction conditions: NMA methanol solution, 150 mL, 0.2 mol/L; H₂ pressure, 0.8 MPa; reaction time, 2 h; reaction temperature, 140 °C; catalyst loading, 1.0 g; and stirring rate, 400 rpm.

Conclusions

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Monometallic Cu, monometallic Ni, and bimetallic Cu_xNi_y nanoparticles with the small particle sizes and narrow size distributions were successfully prepared by the wet chemical reduction method using Tween as the organic modifier and hydrazine hydrate as the reductant. Cu-Ni alloy phase was formed in the bimetallic Cu_xNi_y nanoparticles. The formation of Cu-Ni alloy phase in the bimetallic Cu_xNi_y nanoparticles favored the hydrogenation of NMA with H₂ to AMA. The bimetallic Cu_{0.7}Ni_{0.3} catalyst exhibited good stability without obvious deactivation after recycling for 4 times. A power-function type reaction kinetic model over the bimetallic Cu_{0.7}Ni_{0.3} catalyst well fitted the experimental data, $r_0 = -dn_0/(dt \cdot W_{cat}) = kC_0^{0.45}P_0^{1.15}$, and the reaction activation energy was 19.74 kJ mol⁻¹. The bimetallic Cu_xNi_y nanoparticle catalyst probably has potential application for catalytic

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hydrogenation of other reducible chemicals.

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A table of contents entry



The presence of Cu-Ni alloy phase favored the catalytic hydrogenation of 3-nitro-4-methoxy-acetylaniline to 3-amino-4-methoxy-acetylaniline.