

# Article

# Supported Au-Ni nano-alloy catalysts for the chemoselective hydrogenation of nitroarenes



Haisheng Wei<sup>a,b</sup>, Xing Wei<sup>a</sup>, Xiaofeng Yang<sup>a</sup>, Guangzhao Yin<sup>c</sup>, Aiqin Wang<sup>a,\*</sup>, Xiaoyan Liu<sup>a</sup>, Yangiang Huang<sup>a</sup>, Tao Zhang<sup>a,#</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China <sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

#### ARTICLE INFO

Article history: Received 27 September 2014 Accepted 3 November 2014 Published 20 February 2015

Keywords: Gold-nickel Allov Chemoselective hydrogenation Nitroarenes

#### 1. Introduction

## The chemoselective hydrogenation of nitroarenes is an environmentally benign and high atomic efficiency approach for the synthesis of functionalized anilines, which are important intermediates for the production of herbicides, pesticides, pigments, drugs, and dyes [1]. Transition metals like Pt, Pd, Ru, and Ni are typical catalysts in a variety of hydrogenation reactions, but they suffer from a low chemoselectivity in the hydrogenation of substituted nitroarenes, especially when two or more reducing groups are present in one nitroarene molecule [2-4]. On the other hand, IB group metals are usually poor catalysts for hydrogenation reactions, but have recently been

shown to be highly chemoselective for the hydrogenation of various substituted nitroarenes [4-9]. Corma et al. [4] reported in 2006 that Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> afforded > 95% selectivity at high conversion levels in the chemoselective hydrogenation of 3-nitrostyrene and other substituted nitroarenes. Shimizu et al. [9] found that  $Au/Al_2O_3$  with gold particles of 2.5 nm performed even better than Au/TiO2 and Au/Fe2O3: the selectivity for 3-vinylaniline attained 99% at full conversion of 3-nitrostyrene. They attributed the high chemoselectivity to the unique ability of Au/Al<sub>2</sub>O<sub>3</sub> to cause H<sub>2</sub> dissociation to produce a H<sup>+</sup>/H<sup>-</sup> pair which is preferentially transferred to the polar bonds in the nitro group. In addition to the support effect, the structure and morphology of the catalyst also affects signifi-

# Corresponding author. Tel: +86-411-84379015; Fax: +86-411-84691570; E-mail: taozhang@dicp.ac.cn

#### ABSTRACT

A modified two-step approach was developed for the synthesis of uniform and highly dispersed Au-Ni alloy nanoparticles on a silica support. The supported Au-Ni alloy nanoparticles were investigated for the chemoselective hydrogenation of substituted nitroarenes, which showed a strong synergistic effect between Au and Ni. The best catalyst was AuNi<sub>3</sub>/SiO<sub>2</sub> that afforded a selectivity to 3-vinylaniline of 93.0% at a 3-nitrostyrene conversion of 90.8% after 70 min under mild conditions. © 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author. Tel: +86-411-84379348; Fax: +86-411-84685940; E-mail: aqwang@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21176235, 21203182, 21202163, 21303194, and 21373206) and the Hundred Talents Program of Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

DOI: 10.1016/S1872-2067(14)60254-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 2, February 2015

cantly the chemoselectivity [9–12]. Mitsudome et al. [10] reported that a AgNPs@CeO<sub>2</sub> catalyst with a core-shell structure gave almost complete chemoselectivity for the reduction of nitrostyrenes, and it was far superior to Ag NPs supported on CeO<sub>2</sub>.

Despite a satisfactory chemoselectivity, neither Au nor Ag catalysts have a promising activity. Their activities for chemoselective hydrogenation reactions are one or two magnitudes lower than those of transition metal catalysts due to the intrinsically poor ability of Au and Ag for hydrogen activation [13,14]. This unacceptably low activity significantly limits the practical application of Au and Ag catalysts. In order to improve the catalytic activity of supported Au catalysts while maintaining a high chemoselectivity, a bimetallic strategy of adding a suitable amount of a transition metal to Au was proposed [13,15–18]. The synergism between Au and a second metal has been intensively studied in the last decade with Au-Ag [19-22], Au-Cu [23,24], Au-Pd [25-27], Au-Pt [13], Au-Co [28], and Au-Ni [29]. However, only a few catalysts gave a chemoselective hydrogenation of nitroarenes. Serna et al. [13] reported that the addition of only 100 ppm Pt to a 1.5%Au/TiO2 catalyst resulted in a 20-fold increase in activity while preserving the high chemoselectivity in the hydrogenation of 3-nitrostyrene to 3-vinylaniline. A similar synergistic effect between Pt and Au was also reported for a Pt-on-Au nanostructure in the chemoselective hydrogenation of cinnamaldehyde [30]. For the Au-Pd bimetallic catalyst system, an increase of up to a factor of 3 in activity was observed for the selective hydrogenation of p-chloronitrobenzene to *p*-chloroaniline [16] when Au/Pd was > 20. These examples demonstrated the potential of Au bimetallic catalysts in the chemoselective hydrogenation reactions.

Here, we report the catalytic performance of silica-supported Au-Ni alloy nanoparticles in the chemoselective hydrogennation of a variety of substituted nitroaromatics. Compared with the previously reported Au-Pt and Au-Pd systems, Au-Ni catalysts possess the advantage of low cost and is thereby more competitive for practical applications. However, the miscibility gap between Au and Ni is a significant challenge in the preparation of homogeneous Au-Ni nanoalloy catalysts [31]. In the present work, we used a modified two-step method in which preformed Au nanoparticles induced the preferential deposition of Ni on the Au surface with the assistance of the mild reducing agent, tert-butylamine borane. The resulting Au@Ni core-shell structure was then transformed into a Au-Ni alloy nanophase by reduction in H<sub>2</sub> at elevated temperatures, which was shown by X-ray diffraction (XRD), transmission electron microscopy (TEM), and extended X-ray adsorption fine structure (EXAFS) characterization. The Au-Ni nanoalloy catalysts exhibited excellent activity and selectivity in the chemoselective hydrogenation of substituted nitroarenes to the corresponding anilines.

#### 2. Experimental

#### 2.1. Preparation of the Catalysts

A monometallic Au/SiO<sub>2</sub> catalyst was prepared by the met-

hod in our previous report [19]. On a commercial silica support (Qingdao Ocean Chemical Plant,  $S_{BET} = 467 \text{ m}^2/\text{g}$ ) was grafted 3-aminopropyltriethoxysilane (APTES, 99%, Acros Organics) by refluxing in ethanol at 80 °C for 24 h, followed with washing by ethanol and drying in air. The resulting material was denoted as SiO<sub>2</sub>-APTES. To prepare the Au-Ni bimetallic alloy catalysts, 1 g of SiO<sub>2</sub>-APTES was added into 20 mL HAuCl<sub>4</sub> solution (0.01 mol/L) and stirred for 30 min. After filtration and washing with water, the recovered solid was dispersed in 10 mL water, and 10 mL NaBH<sub>4</sub> solution (0.2 mol/L) was added dropwise under vigorous stirring for the reduction of AuCl<sub>4</sub>-. After stirring for 15 min, the solid was recovered by filtration and thoroughly washed with water to obtain 4.6 wt% Au/SiO<sub>2</sub>. Then the Au/SiO<sub>2</sub> was re-dispersed into 0.05 mol/L Ni(NO<sub>3</sub>)<sub>2</sub> solution with a defined Au/Ni ratio, followed by the addition of 0.1 mol/L tert-butylamine borane solution to reduce Ni2+. After filtration, washing with water, and drying at 80 °C for 12 h, the solid was calcined at 500 °C in air for 6 h and reduced at 550 °C in H<sub>2</sub> for 1 h to obtain the AuNi<sub>x</sub>/SiO<sub>2</sub>-cal and AuNi<sub>x</sub>/SiO<sub>2</sub>cal-red catalysts, respectively (x refers to the atomic ratio of Au to Ni). For comparison, a Ni/SiO2 catalyst was prepared by incipient wetness impregnation of the SiO<sub>2</sub> support with a Ni(NO<sub>3</sub>)<sub>2</sub> solution, followed by the same calcination and reduction treatment as that for the Au-Ni/SiO<sub>2</sub> catalysts.

#### 2.2. Reaction tests

The catalytic testing for the chemoselective hydrogenation of nitroarenes was conducted in an autoclave equipped with a pressure gauge, magnetic stirring system, and water bath. A mixture of nitroarene substrate, solvent, and an internal standard of *o*-xylene with a total volume of 5 mL was put into the autoclave. Then, the autoclave was flushed with 10<sup>3</sup> kPa hydrogen 5 times. After sealing, the autoclave was charged with H<sub>2</sub> to 300 kPa, then heated to 50 °C in a water bath with stirring to initiate the reaction. After reaction, the product was analyzed by GC-MS.

#### 2.3. Characterization

The Au and Ni loadings were measured with an inductively coupled plasma spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corp.). XRD analysis was determined on a PANalytical X' pert diffractometer equipped with a Cu  $K_{\alpha}$  radiation source operated at 40 kV and 40 mA. Temperature-programmed desorption of H<sub>2</sub> (H<sub>2</sub>-TPD) was performed on an Auto Chem II 2920 automatic catalyst characterization system. TEM was carried out using a Tecnai G2 Spirit (FEI) microscope operating at 200 kV. High resolution transmission electron microscopy (HRTEM) was conducted with a Tecnai G2 F30S-Twin (FEI) microscope operating at 300 kV. The chemical composition of individual particles were measured by energy dispersive X-ray spectroscopy (EDS) on a Tecnai G2 F30S-Twin (FEI) electron microscope. X-ray absorption near edge structure (XANES) and EXAFS spectra at the Au LIII edge and Ni K edge were recorded at beamline 14W of Shanghai Synchrotron Radiation Facility, Shanghai, China.

### 3. Results and discussion

#### 3.1. Formation of Au-Ni alloy nanoparticles

It is a challenging task to form a homogeneous Au-Ni alloy due to the large difference in the reduction potential and immiscibility of the two metals at low temperature [31-33]. In our earlier work, we developed a two-step method for the preparation of Au alloy nanoparticles on a silica support including Au-Ag [19-22], Au-Cu [23,24] and Au-Pd [27], in which NaBH<sub>4</sub> was used as the reducing agent in both reduction steps. However, a similar procedure failed in the preparation of Au-Ni alloy nanoparticles because Ni nanoparticles were preferentially formed in the solution rather than on the preformed gold particle surface. Motivated by the noble metal induced reduction (NMIR) method developed by Li and coworkers [34], we modified the two-step method by using a weak reducing agent, tert-butylamine borane, in the second step, which allowed the preferential deposition of Ni nanoparticles on the gold surface based on the NMIR mechanism. The preparation procedure is illustrated in Fig. 1. The following calcination and reduction treatments were to remove APTES and to promote the formation of a homogeneous Au-Ni alloy phase [19].

Fig. 2(a) presents the XRD patterns of the catalyst samples with different Au/Ni ratios. The monometallic Au/SiO<sub>2</sub> sample presented four broad peaks at  $2\theta = 38.4^{\circ}$ ,  $44.2^{\circ}$ ,  $65.1^{\circ}$ , and 77.8° which were assigned to the reflections of the (111), (200), (220), and (311) lattice planes of Au, respectively. The broad peaks indicated the very small size of the Au particles. Using the Scherrer equation with the Au(111) peak, the average particle size of gold was calculated to be 3.3 nm. For the other three Au-Ni<sub>x</sub>/SiO<sub>2</sub>-cal-red samples, the reflection peaks were broader than that of the monometallic Au, indicating that the presence of a second metal Ni suppressed the sintering of the particles during high temperature calcination and reduction. This trend was in agreement with the Au-Ag [19-22] and Au-Cu [23,24] systems. More interestingly, the reflection peaks of the Au-Ni bimetallic samples were shifted to larger degree with an increase in Ni content, as highlighted in the narrow range XRD patterns (Fig. 2(b)). This provided strong evidence for the formation of the Au-Ni alloy phase. It was also noted that there was no peak assignable to the metallic Ni phase, even for the Ni-rich AuNi<sub>3</sub> sample. However, the absence of a monometallic Ni phase in the XRD pattern does not mean that all the Ni species were in the Ni-Au alloy phase because they could exist as highly dispersed Ni that cannot be detected by XRD.

The TEM images in Fig. 3 provided more details of the particle size distribution. The metal particles in all the samples were



**Fig. 2.** XRD patterns in a wide range (a) and in  $2\theta = 30^{\circ}-50^{\circ}$  (b) of the AuNi<sub>\*</sub>/SiO<sub>2</sub>-cal-red catalysts.

uniformly dispersed on the silica support. No very big particles were observed in the different regions of the samples. The histograms in Fig. 4 showed that the average particle size of Au, AuNi<sub>0.33</sub>, AuNi<sub>1</sub>, and AuNi<sub>3</sub> were 3.69, 3.44, 3.28 and 3.41 nm, respectively, which was basically in agreement with that estimated from the XRD data. EDS analysis of individual particles



Fig. 1. Schematic of the procedure for the synthesis of SiO<sub>2</sub>-supported Au-Ni alloy nanoparticles.



Fig. 3. TEM images of the AuNi<sub>x</sub>/SiO<sub>2</sub>-cal-red catalysts.

revealed that the chemical composition (Au/Ni ratio) differed from one particle to another although most particles contained both Ni and Au (Fig. 5). Heterogeneity in composition is ubiquitous for bimetallic particles [35–37], which in turn affects the catalytic performance.

EXAFS is a powerful technique for identifying the formation of an alloy phase [38,39]. Hence, we performed in situ EXAFS on the  $AuNi_3/SiO_2$  sample. To follow the formation of the Au-Ni



Fig. 5. EDS analysis of individual particles of the  $AuNi_3/SiO_2\mbox{-}cal\mbox{-}red$  catalyst.

alloy phase, both the calcined and calcined-reduced samples were characterized. The results are shown in Table 1. For the calcined sample, there were Au-Au and Au-Ni contributions in the Au Lill edge, with the coordination numbers (CNs) of 9.2 and 0.4, respectively, indicating that only a very small fraction of the Ni bonded with Au, while most of the Ni were on the surface of Au particles or existed as a separate monometallic phase. The same conclusion was reached from the result of the Ni K edge. There were three neighboring shells to Ni, which were Ni-Au, Ni-Ni and Ni-O with CN of 0.5, 9.4, and 4.9, respectively, in the AuNi<sub>3</sub>-cal sample. From these results, we concluded that most of the Ni species were NiO on the surface of the Auparticles as a consequence of the high temperature calcination. After reduction in H2 at 550 °C, the Au@NiO hetero-structure changed greatly. At the Au Lin edge, the CN of the Au-Au shell decreased from 9.2 to 5.0, while the CN of the Au-Ni



Fig. 4. Particle size distributions of the AuNi<sub>x</sub>/SiO<sub>2</sub>-cal-red catalysts.

Table 1
EXAFS results of the AuNi <sub>3</sub> /SiO <sub>2</sub> catalysts after calcination and reduction.

Edge &data fitting range	Sample	Shell	CN	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	R-factor
Au L <sub>III</sub> edge	Au foil	Au-Au	12.0	2.86	0.007	0.0009
	AuNi <sub>3</sub> /SiO <sub>2</sub> -cal	Au-Au	9.2	2.83	0.008	0.0026
		Au-Ni	0.4	2.69	0.006	
	AuNi <sub>3</sub> /SiO <sub>2</sub> -cal-red	Au-Au	5.0	2.78	0.006	0.0017
		Au-Ni	3.4	2.62	0.011	
Ni K edge	Ni foil	Ni-Ni	12.0	2.48	0.005	0.0004
-	NiO	Ni-O	6.0	2.06	0.006	0.0016
		Ni-Ni	12.0	2.95	0.006	
	AuNi <sub>3</sub> /SiO <sub>2</sub> -cal	Ni-Au	0.5	2.69	0.001	0.0002
		Ni-Ni	9.4	2.99	0.014	
		Ni-O	4.9	2.06	0.007	
	AuNi <sub>3</sub> /SiO <sub>2</sub> -cal-red	Ni-Au	4.3	2.62	0.008	0.0017
		Ni-Ni	2.3	2.48	0.004	
		Ni-O	2.7	2.06	0.007	
		Ni-Ni	5.8	3.03	0.013	

CN, coordination number of the absorber-backscatterer pair. *R*, the average absorber–backscatterer distance.  $\sigma^2$ , the Debye-Waller factor. The accuracy of the above parameters were estimated as CN, ±20%; *R*, ±1%;  $\sigma^2$ , ±20%;  $\Delta E_0$ , ±20%.  $\Delta k$  and  $\Delta R$  are the data range used for data fitting in *k* space and *R* space, respectively. For Au L<sub>III</sub> edge:  $\Delta k$ : 3.4–12.2 Å<sup>-1</sup>,  $\Delta R$ : 1.6–3.3 Å; For Ni K edge:  $\Delta k$ : 3.3–13.1 Å<sup>-1</sup>,  $\Delta R$ : 1.3–3.0 Å.

shell increased from 0.4 to 3.4, which was indicative of much more alloying. In agreement with this, the Ni-O coordination number showed a clear decrease after reduction. As a consequence, the CN of Ni-Au and Ni-Ni at a distance of 2.48 Å (characteristic of the metal bond of Ni) was much increased. The presence of the Ni-O contribution after reduction implied that a small fraction of Ni strongly interacted with the silica support to from nickel silicate which cannot be reduced. However, this does not contribute to the catalytic activity in the hydrogenation reactions. The same change was reported earlier in the Au-Cu bimetallic system [40].

To summarize, EXAFS results demonstrated that a significant fraction of Ni was alloyed with Au in the AuNi<sub>3</sub> sample. This alloy phase is expected to show a synergistic effect in hydrogenation reactions.

# *3.2.* Synergistic effect in the chemoselective hydrogenation of nitroarenes

To evaluate the catalytic performance of the different Au-Ni catalysts in the chemoselective hydrogenation of nitroarenes, we first studied the chemoselective hydrogenation of 3-nitrostyrene as it is the most demanding reaction owing to the presence of the -NO<sub>2</sub> and -C=C groups in one molecule [2]. The reaction was conducted under mild conditions, reaction temperature of 50 °C and H<sub>2</sub> pressure of 300 kPa. Table 2 shows the results obtained with the Au-Ni<sub>x</sub>/SiO<sub>2</sub> catalysts with various Au/Ni ratios. The monometallic Au/SiO2 catalyst afforded a moderate activity and excellent selectivity to 3-vinylaniline. The conversion and selectivity reached 79.3% and 99.6% after 8 h reaction, respectively. In comparison to Au/SiO<sub>2</sub>, the 4.11%Ni/SiO<sub>2</sub> catalyst was more active but less selective. The conversion and selectivity reached 93.3% and 78.7% after 108 min reaction, respectively. Similar to 4.11%Ni/SiO<sub>2</sub>, commercial Raney Ni also gave poor selectivity. On the other hand, the Au-Ni<sub>x</sub>/SiO<sub>2</sub> bimetallic catalysts gave both high activity and selectivity, demonstrating a strong synergistic effect between the two metals. In particular, with an increase of Ni content in the Au-Ni bimetallic catalysts, the activity increased remarkably while the selectivity remained above 90% at high conversions, implying that Ni contributed mainly to the improvement of the activity while Au preserved the high chemoselectivity. AuNi<sub>3</sub>/SiO<sub>2</sub> showed the best performance. The conversion and selectivity were 90.8% and 93.0% after a reaction time of only 70 min. For a better comparison, we also tested a standard Au/TiO2 catalyst under identical reaction conditions and with the same Au/substrate ratio. In agreement with the literature [9], the Au/TiO<sub>2</sub> catalyst afforded a much better performance than Au/SiO<sub>2</sub>: it took 180 min to obtain 99.6% conversion and 99.1% selectivity. Obviously, the redox property of the TiO<sub>2</sub> support played an important role in this reaction. In comparison to Au/TiO2, our AuNi3/SiO2 catalyst was more active but a little less selective. It can be envisioned that if it was supported on a redox support such as TiO2 or Fe<sub>2</sub>O<sub>3</sub>, the Au-Ni bimetallic catalyst could give a better performance than its counterpart on the SiO<sub>2</sub> support.

#### Table 2

Chemoselective hydrogenation of 3-nitrostyrene over different catalysts.

Catalust	Time	Conversion	Selectivity	TOF <sup>a</sup>
Catalyst	(min)	(%)	(%)	(h-1)
Au/SiO <sub>2</sub>	480	79.3	99.6	5.5
AuNi0.33/SiO2	310	90.5	96.4	19.9
AuNi <sub>1</sub> /SiO <sub>2</sub>	160	92.5	92.1	21.9
AuNi3/SiO2	70	90.8	93.0	17.9
4.11%Ni/SiO2	108	93.3	78.7	25.5
1.37%Ni/SiO2	480	17.3	97.8	2.8
0.46%Ni/SiO2	960	11.2	99.2	1.3
Au/TiO2 <sup>b</sup>	180	99.6	99.1	—
Raney Ni <sup>c</sup>	155	76.8	62.5	_
4.11%Ni/SiO2+Au/SiO2	108	92.9	80.1	_

Reaction conditions: T = 50 °C, P = 300 kPa, 0.1 g catalyst, 0.5 mmol substrate, toluene as a solvent, *o*-xylene as an internal standard. <sup>a</sup> Calculated based on the metal dispersions in Table 3.

<sup>b</sup>Catalyst amount: 0.3 g for the same Au/substrate ratio as Au/SiO<sub>2</sub>.

<sup>c</sup> Catalyst amount: 15 mg Raney Ni + 0.1 g SiO<sub>2</sub> powder.

Table 3 Physical and chemical properties of the AuNi<sub>\*</sub>/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts.

Catalyst	Metal loadi	ng (wt%)	II. untaka (umal /a)	$\mathbf{D}$ is a section $\mathcal{D}(0/2)$	Doutialo aire h (mm)
	Au	Ni	H2-uptake (µmor/g)	Dispersion <sup>a</sup> (%)	i ai ticle size" (IIIII)
Au/SiO <sub>2</sub>	4.54	—	—	27.1	3.69
AuNi <sub>3</sub> /SiO <sub>2</sub>	4.12	3.91	15	29.3	3.41
AuNi <sub>1</sub> /SiO <sub>2</sub>	4.73	1.37	27	30.5	3.28
AuNi <sub>0.33</sub> /SiO <sub>2</sub>	4.70	0.37	12	29.1	3.44
4.11%Ni/SiO2	—	4.11	5	11.4	8.81
1.37%Ni/SiO2	_	1.37	3	16.3	6.13
0.46%Ni/SiO2		0.46	6	35.2	2.84

<sup>a</sup> Estimated from *D* = 1/*d* (*D*: dispersion; *d*: average diameter of particles); <sup>b</sup> Estimate based on more than 200 particles in TEM images.

To further demonstrate the synergy between Au and Ni, we performed a control experiment with a mechanical mixture of Ni/SiO<sub>2</sub> and Au/SiO<sub>2</sub> with the same metal contents as AuNi<sub>3</sub>/SiO<sub>2</sub>, which was denoted as 4.11%Ni/SiO<sub>2</sub>+Au/SiO<sub>2</sub>. The result showed that this physical mixture catalyst performed similarly to the monometallic 4.11%Ni/SiO<sub>2</sub> catalyst, giving a selectivity of 80.2% at a conversion of 92.9%. Clearly, the improvement of the catalytic performance was due to a synergistic effect between the two metals since it was not a simple additive effect.

Another interesting phenomenon was that all the bimetallic Au-Ni catalysts gave higher catalytic activity or selectivity than their monometallic Ni/SiO<sub>2</sub> counterparts at the same Ni content (e.g., AuNi<sub>0.33</sub>/SiO<sub>2</sub> vs. 0.46%Ni/SiO<sub>2</sub>, AuNi<sub>1</sub>/SiO<sub>2</sub> VS. 1.37%Ni/SiO<sub>2</sub>, AuNi<sub>3</sub>/SiO<sub>2</sub> vs. 4.11%Ni/SiO<sub>2</sub>). The characterization results of the bimetallic catalysts have revealed that the Au-Ni nanoalloy phase was formed in these bimetallic catalysts. Even for the AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst that has excess Ni, there was still a significant amount of Ni alloying with Au. The formation of the alloy provided intimate contact between Au and Ni atoms, thus both geometric and electronic effects between the two metals occurred easily. H<sub>2</sub> chemisorption is able to provide useful information on the synergistic effect between the two metals. Table 3 lists the H<sub>2</sub> uptake of the Au-Ni bimetallic catalysts and the monometallic counterpart. Monometallic Au/SiO2 does not adsorb H<sub>2</sub>, which is consistent with that Au is a poor catalyst for hydrogen activation [14]. In contrast, the bimetallic Au-Ni catalysts adsorb H<sub>2</sub> well. The H<sub>2</sub> uptakes were 15, 27, and 12 µmol/g<sub>Cat</sub> for AuNi<sub>3</sub>, AuNi<sub>1</sub>, and AuNi<sub>0.33</sub>, respectively. These H<sub>2</sub> uptake values are remarkably larger than that of their monometallic Ni counterparts. Therefore, the formation of the Au-Ni alloy phase allowed H<sub>2</sub> to be activated more easily, thus enhancing the catalytic activity for the chemoselective hydrogenation of nitroarenes. On the other hand, previous studies on the surface science of the Au-Ni alloy showed that Au is enriched on the surface in a H<sub>2</sub> atmosphere due to its lower surface energy than Ni [29,41], which facilitates the preferential adsorption of the nitro group on the Au surface and then the chemoselective hydrogenation of nitroarenes. As Au does not adsorb H<sub>2</sub>, the metal dispersion was estimated from the average particle size obtained from TEM, rather than from the hydrogen uptake. The results are listed in Table 3. Then, we calculated the TOF (turnover frequency) for the chemoselective hydrogenation of nitroarenes. The results are shown in Table 2. The TOF of the AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst was 3 fold higher than that of Au/SiO2 while preserving

the selectivity above 90%. Although the 4.11%Ni/SiO<sub>2</sub> catalyst afforded an even higher TOF than the AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst, its selectivity to 3-vinylaniline was significantly lower. For the other two monometallic Ni catalysts, the TOF were one order of magnitude lower than the corresponding Au-Ni alloy counterparts. The promising activity and chemoselectivity of Au-Ni bimetallic catalysts can be attributed to the improved H<sub>2</sub> activation and preserving of the preferential adsorption of nitro groups on the gold surface due to synergy between Au and Ni.

Finally, the best performance catalyst AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst was evaluated for the chemoselective hydrogenation of a variety of nitroarene substrates. As shown in Table 4, nitroarens possessing a C=C bond, carbonyl, nitriles, and halogens were all transformed to the corresponding substituted anilines with high chemoselectivity at high conversions, demonstrating the great potential of Au-Ni bimetallic catalysts for this type of reaction.

#### Table 4

Chemoselective hydrogenation of different substituted nitroarenes over  $AuNi_3/SiO_2.$ 

Entw	Cubatrata	Droduct	Time	Conversion	Selectivity
Еппл	Substrate	Product	(min)	(%)	(%)
1	NO <sub>2</sub>	NH <sub>2</sub>	70	90.8	93.0
2	$\downarrow^{NO_2}$ .Cl	$\stackrel{\rm NH_2}{\downarrow}$ .Cl	105	94.8	93.1
3*	NO <sub>2</sub>	$\downarrow^{\rm NH_2}$	100	100	96.5
	Cho				
4*	NC NO2	NC NH2	60	99.5	93.1
5*	NC NO2	NH2	66	97.1	99.3
6*	$\gamma \sim 0$		40	97.0	97.1
0	O		40	57.0	,

Reaction conditions: T = 50 °C, P = 300 kPa, 0.1 g catalyst, 0.5 mmol substrate, toluene as a solvent, o-xylene as an internal standard. \* 0.2 g catalyst, T = 50 °C, P = 300 kPa.



#### 4. Conclusions

Silica-supported Au-Ni alloy nanoparticles with different Au/Ni ratios were prepared with a modified two-step method in which Au nanoparticles were deposited on an APTES- functionalized silica surface in the first step, and Ni was preferentially deposited on the Au surface in the second step by using a weak reducing agent, *tert*-butylamine borane. After calcination and reduction, a Au-Ni alloy phase was formed. The Au-Ni alloy nanocatalysts were highly active and chemoselective for the hydrogenation of substituted nitroarenes to the corresponding anilines. The AuNi<sub>3</sub>/SiO<sub>2</sub> catalyst gave the best performance with a chemoselectivity of 93.0% at 90.8% conversion for 3-nitrostyrene hydrogenation. The enhanced activity was attributed to the improved H<sub>2</sub> dissociation on the Au-Ni alloy phase.

#### Acknowledgments

The authors thank the students and staff at beamline 14W (Shanghai Synchrotron Radiation Facility, Shanghai, China) for their assistance with the EXAFS data collection.

#### References

- Ono N. The Nitro Group in Organic Synthesis. NewYork: John Wiley & Sons, 2003
- [2] Xu K L, Zhang Y, Chen X R, Huang L, Zhang R, Huang J. Adv Synth Catal, 2011, 353: 1260
- [3] Liu H, Li R Y, Zhang M, Li W, Zhang M H, Tao K Y. Chin J Catal, 2009, 30: 606
- [4] Corma A, Serna P. Science, 2006, 313: 332
- [5] Chen Y Y, Qiu J S, Wang X K, Xiu J H. J Catal, 2006, 242: 227
- [6] Chen Y Y, Wang C, Liu H Y, Qiu J S, Bao X H. Chem Commun, 2005: 5298
- [7] Shimizu K I, Miyamoto Y, Satsuma A. J Catal, 2010, 270: 86
- [8] He L, Ni J, Sun H, Cao Y. *Chin J Catal*, 2009, 30: 958
- [9] Shimizu K I, Miyamoto Y, Kawasaki T, Tanji T, Tai Y, Satsuma A. J

Phys Chem C, 2009, 113: 17803

- [10] Mitsudome T, Mikami Y, Matoba M, Mizugaki T, Jitsukawa K, Kaneda K. Angew Chem Int Ed, 2012, 51: 136
- [11] Boronat M, Concepción P, Corma A, González S, Illas F, Serna P. J Am Chem Soc, 2007, 129: 16230
- [12] Cárdenas-Lizana F, Gómez-Quero S, Keane M A. ChemSusChem, 2008, 1: 215
- [13] Serna P, Concepción P, Corma A. J Catal, 2009, 265: 19
- [14] Corma A, Boronat M, González S, Illas F. Chem Commun, 2007: 3371
- [15] He D P, Jiao X D, Jiang P, Wang J, Xu B Q. Green Chem, 2012, 14: 111
- [16] Cárdenas-Lizana F, Gómez-Quero S, Hugon A, Delannoy L, Louis C, Keane M A. J Catal, 2009, 262: 235
- [17] Cárdenas-Lizana F, Gómez-Quero S, Baddeley C J, Keane M A. Appl Catal A, 2010, 387: 155
- [18] Wang A Q, Liu X Y, Mou C Y, Zhang T. J Catal, 2013, 308: 258
- [19] Liu X Y, Wang A Q, Yang X F, Zhang T, Mou C Y, Su D S, Li J. Chem Mater, 2009, 21: 410
- [20] Wang A Q, Liu J H, Lin S D, Lin T S, Mou C Y. J Catal, 2005, 233: 186
- [21] Wang A Q, Hsieh Y P, Chen Y F, Mou C Y. J Catal, 2006, 237: 197
- [22] Wang A Q, Chang C M, Mou C Y. J Phys Chem B, 2005, 109: 18860
- [23] Liu X Y, Wang A Q, Wang X D, Mou C Y, Zhang T. Chem Commun, 2008: 3187
- [24] Li W J, Wang A Q, Liu X Y, Zhang T. Appl Catal A, 2012, 433: 146
- [25] Zhang L L, Wang A Q, Miller J T, Liu X Y, Yang X F, Wang W T, Li L, Huang Y Q, Mou C Y, Zhang T. ACS Catal, 2014, 4: 1546
- [26] Pei G X, Liu X Y, Wang A Q, Li L, Huang Y Q, Zhang T, Lee J W, Jang B W-L, Mou C Y. New J Chem, 2014, 38: 2043
- [27] Wei X, Yang X F, Wang A Q, Li L, Liu X Y, Zhang T, Mou C Y, Li J. J Phys Chem C, 2012, 116: 6222
- [28] Xu X J, Fu Q, Wei M M, Wu X, Bao X H. Catal Sci Technol, 2014, 4: 3151
- [29] Xu X J, Fu Q, Guo X G, Bao X H. ACS Catal, 2013, 3: 1810
- [30] Sun K Q, Hong Y C, Zhang G R, Xu B Q. ACS Catal, 2011, 1: 1336
- [31] Bienzle M, Oishi T, Sommer F. J Alloys Compd, 1995, 220: 182
- [32] Zhou S H, Yin H F, Schwartz V, Wu Z L, Mullins D, Eichhorn B, Overbury S H, Dai S. ChemPhysChem 2008, 9: 2475
- [33] Molenbroek A M, Nørskov J K, Clausen B S. J Phys Chem B, 2001, 105: 5450
- [34] Wang D S, Li Y D. J Am Chem Soc, 2010, 132: 6280

- [35] Xu J, White T, Li P, He C H, Yu J G, Yuan W K, Han Y F. *J Am Chem Soc*, 2010, 132: 10398
- [36] Russier-Antoine I, Bachelier G, Sablonière V, Duboisset J, BenichouE, Jonin C, Bertorelle F, Brevet P F. *Phys Rev B*, 2008, 78: 035436
- [37] Bulushev D A, Beloshapkin S, Plyusnin P E, Shubin Y V, Bukhtiyarov V I, Korenev S V, Ross J R H. J Catal, 2013, 299: 171
- [38] Liu X Y, Wang A Q, Li L, Zhang T, Mou C Y, Lee J F. Prog Nat Sci,

2013, 23: 317

- [39] Yen C W, Lin M L, Wang A Q, Chen S A, Chen J M, Mou C Y. J Phys Chem C, 2009, 113: 17831
- [40] Liu X Y, Wang A Q, Li L, Zhang T, Mou C Y, Lee J F. J Catal, 2011, 278: 288
- [41] Jiang H L, Umegaki T, Akita T, Zhang X B, Haruta M, Xu Q. *Chem Eur J*, 2010, 16: 3132