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Article

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

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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 AuNi₃/SiO₂ that afforded a selectivity to 3-vinylaniline of 93.0% at a 3-nitrostyrene conversion of 90.8% after 70 min under mild conditions.

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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/TiO₂ and Au/Fe₂O₃ 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/Al₂O₃ 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/Al₂O₃ to cause H₂ dissociation to produce a H⁺/H⁻ 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-

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cantly the chemoselectivity [9–12]. Mitsudome et al. [10] reported that a AgNPs@CeO₂ 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 CeO₂.

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 hydrogenation 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 H₂ 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/SiO₂ catalyst was prepared by the met-

hod in our previous report [19]. On a commercial silica support (Qingdao Ocean Chemical Plant, *S*_{BET} = 467 m²/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 SiO₂-APTES. To prepare the Au–Ni bimetallic alloy catalysts, 1 g of SiO₂-APTES was added into 20 mL HAuCl₄ 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 NaBH₄ solution (0.2 mol/L) was added dropwise under vigorous stirring for the reduction of AuCl₄[−]. After stirring for 15 min, the solid was recovered by filtration and thoroughly washed with water to obtain 4.6 wt% Au/SiO₂. Then the Au/SiO₂ was re-dispersed into 0.05 mol/L Ni(NO₃)₂ 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 H₂ for 1 h to obtain the AuNi_{*x*}/SiO₂-cal and AuNi_{*x*}/SiO₂-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 SiO₂ support with a Ni(NO₃)₂ solution, followed by the same calcination and reduction treatment as that for the Au–Ni/SiO₂ 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 10³ kPa hydrogen 5 times. After sealing, the autoclave was charged with H₂ 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_α radiation source operated at 40 kV and 40 mA. Temperature-programmed desorption of H₂ (H₂-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_4 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/SiO₂ sample presented four broad peaks at $2\theta = 38.4^\circ$, 44.2° , 65.1° , 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_x/SiO₂-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 AuNi₃ 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° (b) of the AuNi_x/SiO₂-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_{0.33}, AuNi₁, and AuNi₃ 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 SiO₂-supported Au-Ni alloy nanoparticles.

Fig. 3. TEM images of the $\text{AuNi}_x/\text{SiO}_2$ -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 $\text{AuNi}_3/\text{SiO}_2$ sample. To follow the formation of the Au-Ni

Fig. 5. EDS analysis of individual particles of the $\text{AuNi}_3/\text{SiO}_2$ -cal-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 L_{III} 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_3 -cal sample. From these results, we concluded that most of the Ni species were NiO on the surface of the Au particles as a consequence of the high temperature calcination. After reduction in H_2 at 550 °C, the Au@NiO hetero-structure changed greatly. At the Au L_{III} 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 $\text{AuNi}_x/\text{SiO}_2$ -cal-red catalysts.

Table 1EXAFS results of the AuNi₃/SiO₂ catalysts after calcination and reduction.

Edge & data fitting range	Sample	Shell	CN	<i>R</i> (Å)	σ^2 (Å ²)	<i>R</i> -factor
Au L _{III} edge	Au foil	Au-Au	12.0	2.86	0.007	0.0009
		Au-Ni	0.4	2.69	0.006	
	AuNi ₃ /SiO ₂ -cal	Au-Au	9.2	2.83	0.008	0.0026
		Au-Ni	0.4	2.69	0.006	
		Au-Au	5.0	2.78	0.006	0.0017
Ni K edge	Ni foil	Ni-Ni	12.0	2.48	0.005	0.0004
		Ni-O	6.0	2.06	0.006	0.0016
	AuNi ₃ /SiO ₂ -cal	Ni-Ni	12.0	2.95	0.006	
		Ni-Au	0.5	2.69	0.001	0.0002
		Ni-Ni	9.4	2.99	0.014	
	AuNi ₃ /SiO ₂ -cal-red	Ni-O	4.9	2.06	0.007	
		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	
		Ni-Ni	5.8	3.03	0.013	

CN, coordination number of the absorber-backscatterer pair. *R*, the average absorber-backscatterer distance. σ^2 , the Debye-Waller factor. The accuracy of the above parameters were estimated as CN, $\pm 20\%$; *R*, $\pm 1\%$; σ^2 , $\pm 20\%$; ΔE_0 , $\pm 20\%$. Δk and ΔR are the data range used for data fitting in *k* space and *R* space, respectively. For Au L_{III} edge: Δk : 3.4–12.2 Å⁻¹, ΔR : 1.6–3.3 Å; For Ni K edge: Δk : 3.3–13.1 Å⁻¹, ΔR : 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 form 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 AuNi₃ 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 –NO₂ and –C=C groups in one molecule [2]. The reaction was conducted under mild conditions, reaction temperature of 50 °C and H₂ pressure of 300 kPa. Table 2 shows the results obtained with the Au-Ni_x/SiO₂ 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/SiO₂, the 4.11%Ni/SiO₂ 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/SiO₂, commercial Raney Ni also gave poor selectivity. On the other hand, the Au-Ni_x/SiO₂ bimetallic catalysts gave both high activity and selectivity, demonstrating a strong syn-

ergistic 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. AuNi₃/SiO₂ 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/TiO₂ catalyst afforded a much better performance than Au/SiO₂: it took 180 min to obtain 99.6% conversion and 99.1% selectivity. Obviously, the redox property of the TiO₂ 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 Fe₂O₃, the Au-Ni bimetallic catalyst could give a better performance than its counterpart on the SiO₂ support.

Table 2

Chemoselective hydrogenation of 3-nitrostyrene over different catalysts.

Catalyst	Time (min)	Conversion (%)	Selectivity (%)	TOF ^a (h ⁻¹)
Au/SiO ₂	480	79.3	99.6	5.5
AuNi _{0.33} /SiO ₂	310	90.5	96.4	19.9
AuNi ₁ /SiO ₂	160	92.5	92.1	21.9
AuNi ₃ /SiO ₂	70	90.8	93.0	17.9
4.11%Ni/SiO ₂	108	93.3	78.7	25.5
1.37%Ni/SiO ₂	480	17.3	97.8	2.8
0.46%Ni/SiO ₂	960	11.2	99.2	1.3
Au/TiO ₂ ^b	180	99.6	99.1	—
Raney Ni ^c	155	76.8	62.5	—
4.11%Ni/SiO ₂ +Au/SiO ₂	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.

^a Calculated based on the metal dispersions in Table 3.

^b Catalyst amount: 0.3 g for the same Au/substrate ratio as Au/SiO₂.

^c Catalyst amount: 15 mg Raney Ni + 0.1 g SiO₂ powder.

Table 3Physical and chemical properties of the AuNi_x/SiO₂ and Ni/SiO₂ catalysts.

Catalyst	Metal loading (wt%)		H ₂ -uptake (μmol/g)	Dispersion ^a (%)	Particle size ^b (nm)
	Au	Ni			
Au/SiO ₂	4.54	—	—	27.1	3.69
AuNi ₃ /SiO ₂	4.12	3.91	15	29.3	3.41
AuNi ₁ /SiO ₂	4.73	1.37	27	30.5	3.28
AuNi _{0.33} /SiO ₂	4.70	0.37	12	29.1	3.44
4.11%Ni/SiO ₂	—	4.11	5	11.4	8.81
1.37%Ni/SiO ₂	—	1.37	3	16.3	6.13
0.46%Ni/SiO ₂	—	0.46	6	35.2	2.84

^a Estimated from $D = 1/d$ (D : dispersion; d : average diameter of particles); ^b 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/SiO₂ and Au/SiO₂ with the same metal contents as AuNi₃/SiO₂, which was denoted as 4.11%Ni/SiO₂+Au/SiO₂. The result showed that this physical mixture catalyst performed similarly to the monometallic 4.11%Ni/SiO₂ 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/SiO₂ counterparts at the same Ni content (e.g., AuNi_{0.33}/SiO₂ vs. 0.46%Ni/SiO₂, AuNi₁/SiO₂ vs. 1.37%Ni/SiO₂, AuNi₃/SiO₂ vs. 4.11%Ni/SiO₂). The characterization results of the bimetallic catalysts have revealed that the Au-Ni nanoalloy phase was formed in these bimetallic catalysts. Even for the AuNi₃/SiO₂ 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. H₂ chemisorption is able to provide useful information on the synergistic effect between the two metals. Table 3 lists the H₂ uptake of the Au-Ni bimetallic catalysts and the monometallic counterpart. Monometallic Au/SiO₂ does not adsorb H₂, which is consistent with that Au is a poor catalyst for hydrogen activation [14]. In contrast, the bimetallic Au-Ni catalysts adsorb H₂ well. The H₂ uptakes were 15, 27, and 12 μmol/g_{cat} for AuNi₃, AuNi₁, and AuNi_{0.33}, respectively. These H₂ uptake values are remarkably larger than that of their monometallic Ni counterparts. Therefore, the formation of the Au-Ni alloy phase allowed H₂ 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 H₂ 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 H₂, 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 AuNi₃/SiO₂ catalyst was 3 fold higher than that of Au/SiO₂ while preserving

the selectivity above 90%. Although the 4.11%Ni/SiO₂ catalyst afforded an even higher TOF than the AuNi₃/SiO₂ 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 H₂ 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 AuNi₃/SiO₂ catalyst was evaluated for the chemoselective hydrogenation of a variety of nitroarene substrates. As shown in Table 4, nitroarenes 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 4Chemoselective hydrogenation of different substituted nitroarenes over AuNi₃/SiO₂.

Entry	Substrate	Product	Time (min)	Conversion (%)	Selectivity (%)
1			70	90.8	93.0
2			105	94.8	93.1
3*			100	100	96.5
4*			60	99.5	93.1
5*			66	97.1	99.3
6*			40	97.0	97.1

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

Graphical Abstract

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

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Supported Au-Ni alloy nanoparticles were highly active and chemoselective for the hydrogenation of substituted nitroarenes due to a synergistic effect between Au and Ni. The best catalyst was AuNi₃/SiO₂.

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 AuNi₃/SiO₂ 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 H₂ dissociation on the Au-Ni alloy phase.

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负载型Au-Ni合金催化剂应用于芳香硝基化合物选择加氢反应

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摘要: 采用改进的两步还原法制备了SiO₂负载的Au-Ni合金催化剂, 催化剂中Au-Ni纳米颗粒高度分散于SiO₂载体表面. Au-Ni合金催化剂在温和条件下芳香硝基化合物选择加氢反应中表现出比两种单金属催化剂更高的活性和选择性, 体现出Au-Ni之间明显的协同作用. 其中AuNi₃/SiO₂催化剂具有最好的性能, 反应70 min, 转化率和选择性分别达到90.8%和93.0%.

关键词: 金-镍; 合金; 选择加氢; 芳香硝基化合物

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