

Heterogeneous Catalytic Transfer Partial-Hydrogenation with Formic Acid as Hydrogen Source Over the Schiff-Base Modified Gold Nano-Catalyst

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Abstract The catalytic hydrogenation transformation with gaseous hydrogen in liquid phase always refers to a harsh condition and over-hydrogenation, and it is highly desired to develop new methods with partial-hydrogenation at mild condition. Herein, a heterogeneous catalytic transfer partial-hydrogenation strategy with formic acid as hydrogen source was developed over the Schiff-base modified gold nano-catalysts. The Au/Schiff-SiO₂ catalyst was successfully prepared by one pot aldimine condensation and NaBH₄ reduction of a gold precursor. The characterization results indicated that the gold nanoparticles with an average size below 2 nm were highly dispersed over the Schiff-base modified silica support. Such Schiff-based gold nano-catalysts exhibits excellent activity and partial-hydrogenation selectivity, with a high yield (>99%) for phenylacetylene partial-hydrogenation and achieving a 75% chemoselectivity for imines at a relative low temperature and atmospheric pressure. More importantly, the excess of formic acid can be removed by the direct dissociation of formic acid over Au/Schiff-SiO₂ catalyst with CO₂ emission into atmosphere, which leads to a hydrogen source as clean as hydrogen gaseous, but with a much more high activity and selectivity under mild reaction process.

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1 Introduction

The hydrogenation transformation is used widely as a basic process in organic chemistry and fine-chemical synthesis [1–3]. Admittedly, the hydrogenation with gaseous H_2 as hydrogen source is an effective method, but with a harsh reaction environment (generally with high pressure and temperature) due to the hard solubility of H_2 into the liquid phase, which not only limits its reactivity in its hydrogenation, but also leads to a dangerous experiment operation [4–6]. Therefore, it is highly desired to develop a new method which could not only be efficient for hydrogenation transformation but also under mild reaction condition.

Catalytic transfer hydrogenation (CTH) has attracted much recent interest, which provides an in situ hydrogen source from hydrogen donors, such as propanol, cyclohexadiene, etc., and serves as an attractive alternative to the reactions with gaseous molecular hydrogen [7–11]. With the merit of hydrogen source in liquid phase, the hydrogenation transformation can occur at a reaction conditionfriendly and with a promoted catalytic reactivity. However, the import of sacrificial hydrogen donors which will be oxided as a residual in the reaction system, which will lead to the contamination of products and increase the separating cost for product purification. As a practical application view, it is highly to conduct catalytic transfer hydrogenation at a heterogeneous condition with a hydrogen source as clean as gaseous hydrogen.

Among different hydrogen sources, formic acid was considered as the most promising candidate, which can not only provide high throughput of hydrogen atoms, but also avoid the contamination of products by releasing the CO_2 into gas phase [12–18]. However, the production of hydrogen from formic acid always needs basic additives, such as triethylamine or formic salts. Fortunately, in our previous research, we have found that the Schiff-base modified gold nanocatalysts showed excellent catalytic performances for H₂ production in catalytic dehydrogenation of high-concentration FA without any additive [19]. More importantly, the gold nanocatalyst is generally considered as an effective catalyst for the partial hydrogenation in various organic functional synthesis. Therefore, inspired by our previous work on the dehydrogenation of formic acid as well as the partial chemo selectivity properties of gold nano-catalysts, we reported here a formic acid-mediated CTH of phenylacetylene (PA) to Styrene (ST) and the synthesis of imines compound from the reduction-coupling of nitroarenes and carbonyl using the Schiff-base modified gold as catalyst, which provides a new route for the partial-hydrogenation in fine-chemical synthesis.

2 Experimental

2.1 Catalyst Synthesis

2.1.1 Au/Schiff-SiO₂

The Au/Schiff-SiO₂ catalyst was successfully prepared by one pot aldimine condensation and NaBH₄ reduction of a gold precursor according to our previous reported procedure [19]. Briefly, 10 mL HCHO solution (37%) and 4.5 g APTES (3-aminopropyltriethoxysilane) was added into 150 mL deionized water with stirring for 2 h at room temperature, and then the slurry was filtered, washed thoroughly with deionized water and dried in oven overnight to obtain the Schiff base modified SiO₂ powders (denoted as Schiff-SiO₂). For obtaining the Au/Schiff-SiO₂ catalyst, 1.0 g Schiff-SiO₂ powders and 3.1 mL HAuCl₄·4H₂O (0.01 g/mL) solutions were added into 150 mL deionized water under vigorous stirring for 2 h, then put appropriate NaBH₄ into the above solutions, continue to stir for 2 h before filtered and washed thoroughly with deionized water. The mixture was transferred into Teflon lined autoclave and maintained at 105 °C overnight, and then the precipitate was filtered, washed thoroughly with deionized water and dried in vacuum at 120 °C for 12 h. The Pd/Schiff-SiO₂, Pt/ Schiff-SiO₂ and Ag/Schiff-SiO₂ were prepared in the same manner.

2.1.2 Au/TiO₂

The Au/TiO₂ catalyst was prepared according to the literature [12]. Briefly, the aqueous solutions of HAuCl₄ was heated to 80 °C under vigorous stirring. Using the dropwise addition of NaOH (0.2 M) to tune the pH of 7.0, then put 1 g TiO₂ (P25) into the solution, meanwhile, keeping the pH at 7.0. Before the suspension cooled to room temperature (25 °C), the mixture was stirred for another 2 h at the same temperature. The precipitate was washed with deionized water until the free of chloride ions. The samples were dried under vacuum at room temperature for 12 h and then calcined in air at 350 °C for 2 h.

2.1.3 Au/SBA-15-Amine

The Au/SBA-15-Amine catalyst was prepared according to the literature [19]. Briefly, 1.0 g of SBA-15 and 2.1 mmol of APTES were mixed and stirred thoroughly in 150 mL of anhydrous ethanol for 12 h at 80 °C, aim to graft the surface of SBA-15 with primary amine moieties. After filtration and washed with ethanol, "SBA-15-Amine" was obtained by drying in vacuum at 120 °C for 12 h. Au nanoparticles (NPs) supported on the surface of SBA-15-Amine were prepared by the same synthetic procedure as that for Au/ Schiff-SiO₂ catalyst, and the obtained catalyst was denoted as Au/SBA-15-Amine.

2.2 Characterizations

The actual gold loading of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). High-angle annual dark-filed scanning transmission electron microscopy (HAADF-STEM) images were recorded on a FEI Tecnai G2 F30 S-Twin microscope that was operated at 300 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and drops of the suspension were deposited onto a clean carbon-enhanced copper grid and then dried in air. Power X-ray diffraction (XRD) analysis was carried out on a PW3040/60 X'Pert PRO (PANalytical) diffract meter (CuK_a X-ray source, operated at 40 kV and 50 mA). The Fourier transform infrared (FT-IR) spectroscopy were acquired with a spectrometer (Bruker tensor 27) equipped with a DLATGS detector and operated at a resolution of 4 cm⁻¹. The UV–Vis absorption spectra in solution state and in film state were taken on Agilent Cary 5000 spectrophotometer. The product result was analysed by GC-FID Shanghai Tianmei, GC7890II equipped with an HP-5 column (30 m×0.32×0.25 mm) using anisole as internal standard. The injection-port temperature was 270 °C, the detector temperature was 250 °C, and the initial oven temperature was held at 100 °C and hold for 3 min, then with the heating rate 20 °C min⁻¹ to final 250 °C, keeping 4 min.

2.3 Catalytic Test

2.3.1 The CTH of Phenylacetylene to Styrene

A solvent (10 mL) solution of PA (1 mmol), formic acid (0.5 mL), anisole (1 mmol, the internal standard) and catalyst (1.5 mol% metal) was put into a three-necked flask (50 mL) with a reflux condenser. The resulting mixture was vigorously stirred in a thermostatic oil bath at set temperature.

2.3.2 The CTH of Nitrobenzene and Benzaldehyde to Imines

A mixture of nitrobenzene (1 mmol), benzaldehyde (1 mmol), formic acid (10 mmol), catalyst (1.5 mol % metal), solvents (10 mL) and anisole (1 mmol, the internal standard) were charged into a 50 mL three-necked flask with a reflux condenser. The resulting mixture was vigor-ously stirred in a thermostatic oil bath at set temperature.

3 Results and Discussion

Figure 1 shows the XRD pattern of fresh Au/Schiff-SiO₂ with a metal loading of 2.57 wt% (determined from ICP-AES). No peak of Au was detected and only the diffraction peak of amorphous silica was observed, implying that the gold particles are highly dispersed on the support. In order to clearly examine the metal particle size and size distribution of the gold catalysts on the support, HAADF-STEM technique was employed. From the HAADF-STEM images of 2.57 wt% Au/Schiff-SiO₂ (Fig. 2), the gold NPs were homogeneously dispersed on the support with an average size below 2 nm $(1.75 \pm 0.3 \text{ nm})$, which is in well agreement with the XRD results. It is worth mentioning that the gold NPs do not change a lot after five times of recycles $(1.82 \pm 0.3 \text{ nm})$ in the acid environment. Correspondingly, from the UV-vis spectrum (Fig. 3), the characteristic peak maximum at 530 nm derived from the surface plasmon



Fig. 1 XRD patterns of a Schiff-SiO₂ support; b fresh Au/Schiff-SiO₂

resonance (SPR) of the Au NPs with size >2 nm cannot be well distinguished. In order to clarify the surface moieties of our catalysts, we have performed FT-IR spectra of the fresh 2.57 wt% Au/Schiff-SiO₂ (as seen in Fig. 4). The absorption bands at 2935 and 2872 cm⁻¹ are assigned to asymmetric and symmetric vibrations of the –CH₂ groups in the propyl chain of the APTES, respectively, while the band at 917 cm⁻¹ can be assigned to (–NH) moiety. In addition, a remark peak at 1659 cm⁻¹, ascribed to the stretching vibration of Schiff base (–N=C) is observed, which means that the Schiff base is successfully grafted on the surface of support. Therefore, the gold nano-catalyst with an average size below 2 nm over the Schiff-base modified silica support is successful synthesised.

The unique catalytic transfer hydrogenation performances of such Schiff-base modified gold nano-catalysts have been tested in the partial-hydrogenation of PA and the synthesis of imines from nitroarenes and carbonyl, using formic acid as hydrogen source. Styrene is an important monomer in the production of polystyrene, which serves as a widely used class of thermoplastic [20-23]. Commercial ST produced from the direct dehydrogenation of ethylbenzene generally contains a trace of PA, which has negative impact on the polymerization of ST monomers, and will also induce undesired cross-liking polymer chains [24, 25]. Therefore, it is required to reduce the level of PA to <10 ppm before polymerization via a partial hydrogenation process [26–28]. As seen in Table 1, we have tested the catalytic performance of Au/Schiff-SiO₂ catalysts at different reaction temperatures and compared with other different catalysts in the CTH of PA without additives. It can be seen that Au/Schiff-SiO₂ shows excellent performances (entry 4, Table 1), which achieves a nearly 100% yield to



Fig. 2 HAADF-STEM image of Au/Schiff-SiO₂ a fresh; b used

ST at 60 °C without basic additives. As far as we know, this is the first report to the formic acid mediated CTH of PA to ST without any additives, comparing with the previous researches [29–34]. When gold NPs supported on other supports, such as TiO₂ (P25) or amine-functionalized SBA-15, the conversion of PA is neglectable at the same reaction condition (entry 7 and 8, Table 1). Even for the commercial Pd/C hydrogenation catalyst (from Alfa Aesar), there is almost no conversion of PA at the same reaction condition (entry 9, Table 1). However, the as-prepared Pd/Schiff-SiO₂ (<10% conversion of PA) shows higher activity than the commercial Pd/C catalyst, suggesting that the Schiff base on the support promotes CTH of PA (entry 10, Table 1). In fact, in our previous report [19], we have found that the Schiff base on the support plays an important role on the

hydrogenation production from formic acid. The catalytic performance with H_2 gaseous as hydrogen source, as shown in Table 1 entry 11 and 12 indicated that when at the same reaction condition with formic acid as hydrogen source, no conversion of PA occurs; until only raising up to 120 °C, the conversion of PA can be achieved at 91% with 99% ST selectivity. Therefore, the hydrogen atom is directly transferred from formic acid to the PA substrate over Au/Schiff-SiO₂ catalyst rather than using the formation of H₂ as hydrogen production were suppressed due to the in-situ hydrogenation of PA during formic acid decomposition (as seen in Fig. 5).

We have also analysed the evolution of conversion/selectivity with reaction time for CTH of PA with FA over Au/



Fig. 3 UV–Vis spectra of a Schiff-SiO₂ support; b fresh Au/Schiff-SiO₂



Fig. 4 FT-IR spectra of a Schiff-SiO₂ support; b fresh Au/Schiff-SiO₂

Schiff-SiO₂ catalyst. As depicted in Fig. 6, the formation of ST keep its excellent selectivity (>99%) even the complete conversion of PA. The hydrogenation rate decreases with increasing the reaction time. The conversion rate in the first 30 min is clearly faster than the next 30 min, which might be explained by the prior adsorption of HCOOH to the catalyst so that the adsorption/activation of PA happens at the cost of the decomposition of HCOOH. We have also perforemed catalytic testing with other solvent, including ethanol, toluene, and cyclohexane, as seen in entry 13–15 in Table 1. It was found that such Au/Schiff-base catalysts can always achieve an extra high chemoselectivity toward ST, irrespective of solvent used. As a result, such gold nanocatalyst is intrinsic preference toward the chemoselectivity ity hydorgenation of PA to ST, which might be caused by

tion									
Entry	Catalyst	T (°C)	Solvent	Con. ^b (%)	Sel. ^b (%)				
1	Au/Schiff-SiO ₂	25	n-Hexane	8	>99				
2	Au/Schiff-SiO ₂	40	n-Hexane	16	>99				
3	Au/Schiff-SiO ₂	50	n-Hexane	61	>99				
4	Au/Schiff-SiO ₂	60	n-Hexane	>99	>99				
5	Au/Schiff-SiO ₂	70	n-Hexane	88	91				
6	Schiff-SiO ₂	60	n-Hexane	-	-				
7	Au/SBA-15- amine	60	n-Hexane	Trace	82				
8	Au/TiO ₂	60	n-Hexane	-	-				
9	Pd/C (alfa aesar)	60	n-Hexane	Trace	59				
10	Pd/Schiff-SiO ₂	60	n-Hexane	8	60				
11 ^a	Au/Schiff-SiO ₂	60	n-Hexane	-	-				
12 ^a	Au/Schiff-SiO ₂	120	n-Hexane	90	>99				
13	Au/Schiff-SiO ₂	60	Ethanol	90	95				
14	Au/Schiff-SiO ₂	60	Toluene	92	>99				
15	Au/Schiff-SiO $_2$	60	Cycloheaxne	87	>99				

 Table 1
 Catalytic performance of various catalysts in PA hydrogenation

Reaction condition: 1 mmol PA, 0.5 mL HCOOH, 10 mL n-hexane, metal (1.5 mol%), 1 h

^aReaction condition: 1 mmol PA, 10 mL n-hexane, metal (1.5 mol%), 1 MPa H₂, 1.5 h

^bThe conversion and selectivity were determined by GC using anisole as the internal standard



Fig. 5 The decomposition of formic acid over the Au/Schiff-SiO₂ without PA (*filled square*); with PA existing (*filled circle*). Reaction condition: 0.5 mL HCOOH, 10 mL n-hexane, metal (1.5 mol%), 60 °C, 1 h

its precedence toward PA activation and its inert bebavior toward ST chemosorption.

Finally, in order to evaluate the industrial applicability of such Au/Schiff-SiO₂ catalysts in the purify process of



Fig. 6 Time-conversion/selectivity plot for the CTH of PA over Au/ Schiff-SiO₂. Reaction condition: 1 mmol phenylacetylene, 13 mmol HCOOH, 10 mL n-hexane, metal (1.5 mol%), 60 °C

ST monomers, we have also performed the CTH of PA in a non-solvent system with 1 mmol PA in a large amount of ST (10 mL) (Scheme1). The loss of ST was <2.8%, indicating that this Au/Schiff-SiO₂ can be a good choice in the removal of the tiny amount of PA in the ST feedstock. In addition, the excess FA can be further decomposed thoroughly and the produced water can also be easily separate from the target products, serving as a green process for ST purification.

The catalytic transformation of nitroarenes and carbonyl compounds to imines is wildly used in industry since imines and their derivatives are important chemical intermediates for variegated applications on pharmacy, fine chemistry and agro chemistry [35–39]. Up to now, however, there are only a few reports for the formation of imines from nitroarenes and carbonyl compounds with molecular H₂ as hydrogen source [40, 41]. Aim to acquire a reaction condition-friendly environment, the aqueous-methanol or CO/H₂O as the hydrogen source to replace molecule H₂ have been reported [42, 43].

Here, we try to use formic acid as the hydrogen source for imines synthesis over the Au/Schiff-SiO₂ catalysts (Scheme 2). As seen in Table 2, we have tested the catalytic performance of Au/Schiff-SiO₂ catalysts compared with other different catalysts. It can be seen that the Au/ Schiff-SiO₂ catalyst achieved 75% selectivity to imines with 91% conversion of nitrobenzene (entry 6, Table 2). While Ag/Schiff-SiO₂ and Pt/Schiff-SiO₂ have no activity in the synthesis of imines (entry 1 and 3, Table 2). Pd/ Schiff-SiO₂ showed a low activity and it was easily to overhydrogenation to get N-phenylbenzylamine (4a) (entry 2, Table 2). The effect of temperature was investigated over Au/Schiff-SiO₂ catalysts (entry 4–7, Table 2). The results showed that 70 °C was the preferable temperature for this reaction, The main by-product nitrones (5a) was emerged at lower temperature (50 °C), which needs to continue hydrodeoxygenation to get the imines. While at higher temperature (90 °C), dehydrogenation of formic acid become very fast and nitrobenzene (1a) was reduced to aniline (6a) easilv. As we know, the kinds of solvent may influence on the catalytic performance. Several common organic solvents



Scheme 2 CTH of nitrobenzene and benzaldehyde for the synthesis of imines

Table 2 Experimental resultsof the synthesis of iminesfrom nitrobenzene (1a) andbenzaldehyde (2a)

Entry	Catalyst	T (°C)	Solvent	Con. ^b (%)	Selectivity			
					<u>3a</u>	4a	5a	6a
1	Ag/Schiff-SiO ₂	70	Toluene	n.r.	_	_	_	_
2	Pd/Schiff-SiO ₂	70	Toluene	21	60	30	0	10
3	Pt/Schiff-SiO ₂	70	Toluene	n.r.	_	_	_	_
4	Au/Schiff-SiO ₂	25	Toluene	n.r.	_	_	_	_
5	Au/Schiff-SiO ₂	50	Toluene	72	43	21	28	8
6	Au/Schiff-SiO ₂	70	Toluene	91	75	15	5	5
7	Au/Schiff-SiO ₂	90	Toluene	87	45	30	2	23
8	Au/Schiff-SiO ₂	70	n-Heptane	37	53	12	30	5
9	Au/Schiff-SiO ₂	70	n-Hexane	33	7	12	12	6
10	Au/Schiff-SiO ₂	70	Cyclohexane	72	64	12	21	3
11 ^a	Au/Schiff-SiO ₂	70	Toluene	n.r.	_	_	_	_
12 ^a	Au/Schiff-SiO ₂	120	Toluene	92	91	4	5	0
13 ^a	Pd/Schiff-SiO ₂	120	Toluene	85	2	90	0	8

Reaction condition: nitrobenzene (1 mmol), benzaldehyde (1 mmol), FA (10 mmol), catalyst (1.5 mol% Au), solvent (10 mL), 40 min

^aReaction condition: nitrobenzene (1 mmol), benzaldehyde (1 mmol), H_2 (2 MPa), catalyst (1.5 mol% Au), solvent (10 mL), 2 h

^bGC analysis using anisole as internal standard. Conversion is based on nitrobenzene. n.r. no reaction

were investigated over Au/Schiff-SiO₂ (entry 6 and 8–10, Table 2). The results showed that toluene and cyclohexane as solvent benefits much to achieve imines. We have also tested the catalytic performance with H₂ gaseous as hydrogen source, as shown in Table 2 entry 11 and 12. It was found that no conversion of nitrobenzene occurs at the same reaction condition. The conversion of nitrobenzene can be achieved at 92% with 91% selectivity to imines until the reaction conditions raised up to higher temperature (120 °C), higher pressure (2 MPa) and prolonged the reaction time (2 h).

4 Conclusions

In summary, a partial-hydrogenation strategy was developed with formic acid as hydrogen source over the Schiff base modified gold catalyst with many merits in catalytic transformation. First, the excess of formic acid can be removed by the direct dissociation of formic acid over Au/ Schiff-SiO₂ catalyst with CO₂ emission into atmosphere, which leads to a hydrogen resource as clean as hydrogen gaseous, but with a much more high activity and selectivity under mild reaction process. Second, such Schiff-based gold nano-catalysts exhibits excellent activity and partialhydrogenation selectivity, with a high yield (>99%) for phenylacetylene partial-hydrogenation, and achieving a 75% chemoselectivity for imines at a relative low temperature and atmospheric pressure. Our result will provide a new method for green, reaction condition-friendly, and efficient synthesis of partial-hydrogenation in heterogeneous catalysis.

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