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# Effects of divalent metal ions of hydrotalcites on catalytic behavior of supported gold nanocatalysts for chemoselective hydrogenation of 3-nitrostyrene

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## ABSTRACT

The effect of the divalent metal ions on the hydrotalcite (HT) (MAI-HT; M = Mg, Zn, Ni)-supported thiolated Au<sub>25</sub> nanoclusters (NCs) as the precatalysts for the chemoselective hydrogenation of 3-nitrostyrene to 3-vinylaniline was investigated. The highest chemoselectivity was obtained over the Au<sub>25</sub>/ZnAl-HT-300 (calcined at 300 °C) catalyst, with a maintained selectivity of desired product above 98%. The Au<sub>25</sub>/NiAl-HT-300 catalyst exhibited the highest activity, although the particle size of gold (3.2 nm) was greater than those of the Au<sub>25</sub>/MgAl-HT-300 (2.2 nm) and Au<sub>25</sub>/ZnAl-HT-300 (1.7 nm) catalysts. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results of CO adsorption revealed that Ni interacting intimately with gold could be reduced easily, which affected the catalytic behavior of the Au<sub>25</sub>/NiAl-HT-300 catalyst. Furthermore, the results of the in situ DRIFTS of the adsorption of nitrostyrene at 10 bar of hydrogen suggested that, besides the condensation route, it also followed the direct route to produce aniline on Au<sub>25</sub>/NiAl-HT-300, which was different from the other two catalysts. This work provides new insight into the support effect over the gold catalysts for selective hydrogenation reactions.

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## 1. Introduction

Functionalized aromatic amines are generally produced by selective hydrogenation of the corresponding nitro compounds. They are important industrial intermediates for the production of a range of pharmaceuticals, polymers, agrochemicals, herbicides, dyestuffs, and fine chemicals [1-7]. It was reported that the supported gold catalysts exhibited high chemoselectivity for the hydrogenation of the functionalized nitroaromatics [8–11]. It was proved that the hydrogenation reaction happened at the interfaces between gold and the support [12,13]. Thus, the catalytic performance of the gold catalysts for this reaction could be greatly affected by the nature of the support [9,12–14].

Boronat et al. [9] reported that, over the Au/TiO<sub>2</sub> catalyst, the nitro group instead of the olefinic group could be preferentially adsorbed at the interfaces between gold and the support, which enabled the catalyst to exhibit high chemoselectivity for the hydrogenation of the nitro group. However, such superior adsorption was not observed over the Au/SiO<sub>2</sub> system, which made it not

\* Corresponding author. E-mail address: xyliu2003@dicp.ac.cn (X.Y. Liu). chemoselective for the reduction of substituted nitroaromatic compounds. Compared with the MgO and SiO<sub>2</sub> supports, the Al<sub>2</sub>O<sub>3</sub>-supported gold nanocatalyst with small gold particle size  $(\sim 2.7 \text{ nm})$  was reported to exhibit the best catalytic activity for the selective hydrogenation of 4-nitrostyrene [12]. The coordinatively unsaturated Au atoms on gold nanoparticles (NPs) and the base-acid sites on Al<sub>2</sub>O<sub>3</sub> were claimed to be responsible for the activation of H<sub>2</sub> [12]. Although the support itself was not active for the hydrogenation reaction, it played an important role in affecting the reactivity and selectivity of the gold catalysts. Therefore, it is necessary to investigate the support effect for better understanding of the catalytic mechanism and the rational design of efficient gold catalysts.

Controlling the size of the gold NPs is very important for studying the support effect [15,16]. Recently, thiolated Au<sub>25</sub> NCs appeared as representative precursors for synthesizing supported gold catalysts, because they could be synthesized easily, and the size fit in the interest of the gold catalysis for many redox reactions [17-27]. Previously, we developed a gold catalyst with high chemoselectivity to 3-vinylaniline in the hydrogenation of 3nitrostyrene using ZnAl-HT supported thiolated Au<sub>25</sub> NCs as a precatalyst [28]. We found that, unlike other gold catalysts [9,12]. The





JOURNAL OF CATALYSIS

nitro group and the vinyl group were not competitively adsorbed onto the surface of the Au<sub>25</sub>/ZnAl-HT catalyst, while only the former could be adsorbed and hydrogenated. However, the intrinsic origin of the high chemoselectivity for this catalyst is not yet clear.

In order to gain deep insight into this question, in this work, we tried to study the support effect on the catalytic performance of gold for this reaction. Unlike the previous study on the support effect for the chemoselective hydrogenation of functionalized nitroaromatics over gold catalysts, we used three different hydrotalcites (MAI-HT, M = Mg, Zn, Ni) with similar structures as support precursors. We selected atomically precise thiolated Au<sub>25</sub> NCs as the precursor of gold to exclude the influence of the preparation method on the formation of gold particles. The performance of the three catalysts for the chemoselective hydrogenation of 3-nitrostyrene was obviously different.

A series of characterizations were employed to explore the key factors influencing the catalytic performances. High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) was used to figure out the size distributions of the Au particles.  $CO_2$  temperature-programmed desorption ( $CO_2$  TPD) and in situ DRIFTS of CO adsorption were utilized to test the surface properties of the catalysts. The reaction routes were investigated by in situ DRIFTS of 3-styrene adsorption at 10 bar of H<sub>2</sub>. The reasons that led to the different catalytic performances of the three catalysts were discussed based on the above results. This work will be beneficial for understanding the origin of chemoselectivity and activity over supported gold catalysts for this kind of reactions.

### 2. Experiment

# 2.1. Preparation of the catalysts

The Au<sub>25</sub> NCs were prepared by a NaOH-mediated NaBH<sub>4</sub> reduction method according to the previous work [21,28]. Typically, 5.0 mL of the aqueous solution of HAuCl<sub>4</sub> (110 mM) and 150 mL of cysteine solution (5.5 mM) were successively added to 200 mL of ultrapure water under stirring. Then 30 mL of 1 M NaOH solution was introduced into the above mixture. After 15 min of stirring, excessive sodium borohydride was added to the above solution, followed by vigorous stirring for 3 h. Finally, the products were collected and washed with ethanol-water (V/V = 3:1). The Au<sub>25</sub> NCs were then obtained by lyophilization. The UV-vis spectrum of the Au<sub>25</sub> NCs is shown in Fig. S1 in the Supplementary Information.

The MAI-HTs were prepared as follows. Solution A was obtained by adding  $M(NO_3)_2$ ·6H<sub>2</sub>O (0.21 mol) and  $Al(NO_3)_3$ ·9H<sub>2</sub>O (0.07 mol) to 200 mL of ultrapure water. Solution B was prepared by adding NaOH (0.438 mol) and Na<sub>2</sub>CO<sub>3</sub> (0.113 mol) to 200 mL of ultrapure water. Then solution A was slowly pumped into solution B (3 mL/ min) under constant stirring in the water bath at 75 °C. The gel was aged at 75 °C for 24 h and the solid obtained was filtered and washed with water and ethanol until the pH value of the filtrate became neutral. The precipitates were dried in an oven at 80 °C overnight to obtain the MAI-HTs.

The supported Au<sub>25</sub> NCs catalysts were prepared as follows. Au<sub>25</sub> NCs (30 mg) were dispersed into 10 mL of ultrapure water. Then 2.00 g of the MAI-HT supports was added into the above suspension under vigorous stirring. After 1 h, the product was washed with ultrapure water and collected by centrifugation (8000 rpm, 6 min). The residue was then freeze- dried for 10 h. The obtained samples were defined as Au<sub>25</sub>/MAI-HT. Before the catalytic test, the precursors were calcined at 300 °C for 2 h, with a heating rate of 5 °C/min, and were denoted as Au<sub>25</sub>/MAI-HT-300. The loadings of Au in the Au<sub>25</sub>/MAI-HT-300 catalysts were determined by inductively coupled plasma spectrometry (ICP-AES). They were 1.02, 0.96, and 1.06% when the M was Mg, Zn, and Ni, respectively. To get a good signal/noise ratio, the loading of Au was increased to 10 wt% for characterization by energy-dispersive X-ray mapping (EDS-mapping) and XAS.

For comparison, the Au/MAI-HT-300 catalysts were prepared by the deposition–precipitation (DP) method. In a typical synthesis, an aqueous solution of HAuCl<sub>4</sub> (20 mM, 5 mL) was added to the suspension solution under vigorous stirring, in which 2.00 g of the hydrotalcite powder (MAI-HT) was included. Then 1 M of NaOH solution was used to adjust the pH value to 10. The reaction was allowed to proceed at room temperature for 12 h. Then a solid was obtained after filtering, washing, and drying. Before the catalytic test, the solids were calcined at 300 °C for 2 h, with a heating rate of 5 °C/min.

#### 2.2. Catalytic test

Catalytic testing of the chemoselective hydrogenation of 3nitrostyrene was carried out in a stainless steel autoclave equipped with a pressure gauge under magnetic stirring. Before reaction, a mixture of 3-nitrostyrene (0.2 M) and toluene and o-xylene (0.1 M) totaling 2 mL was put into the vessel. Then certain amounts of catalysts were introduced into the autoclave. After sealing, the autoclave was flushed with hydrogen six times and then pressurized at 10 bar. To initiate the reaction, the reactor was heated to 90 °C in a water bath without stirring until the temperature reached the specified value. After reaction, the product was condensed and analyzed by gas chromatography/mass spectrometry. The turnover frequency (TOF) was measured when the conversion of the substrate was below 20% and calculated in consideration of the total loading of gold [10,28–30] and also its dispersion [31].

### 2.3. Characterization

The actual Au loadings were measured with an ICP-AES on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The UV-visible spectra were recorded on a Cintra (GBC) apparatus with water as a reference at room temperature. The Au<sub>25</sub> NCs were dissolved in the water for measurement. A continuous mode was used in the wavelength range from 190 to 900 nm at a scanning speed of 100 nm min<sup>-1</sup>. The X-ray powder diffraction (XRD) patterns were determined on a PW3040/60 X'Pert PRO (PANalytical) diffractometer equipped with a CuK $\alpha$  radiation source ( $\lambda$  = 0.15432 nm) operating at 40 kV and 40 mA. The HAADF-STEM, the high-resolution transmission electron microscopy (HRTEM), and the EDS mapping images were recorded on a JEOL JEM-2100F microscope equipped with STEM dark-field (DF) and Oxford detectors at 200 kV. CO<sub>2</sub> TPD was conducted on a Micromeritics AutoChem II 2920 automated catalyst characterization system. The CO<sub>2</sub> molecules were detected by an OmniStar mass spectrometer (MS) equipped with the software quadstar 32-bit.

The in situ CO-DRIFTS spectra were acquired with a BRUKER Equinox 55 spectrometer equipped with a MCT detector in the range 400–4000 cm<sup>-1</sup>. An attenuated total reflection infrared (ATR-IR) spectroscope was equipped with a DLaTGS detector and the spectrum was acquired with a Bruker Vertex 70 V spectrometer. The experiment was operated at room temperature and atmospheric pressure. Before the test, the catalyst was dispersed into 10% of the ethanol/water and the mixture treated with ultrasound for 30 min. Then the suspension was added dropwise onto the surface of the diamond crystal on the instrument at a temperature of 90 °C. After drying, the background spectrum was recorded and the substrate solution was added. To get the signal of the adsorbed substrates, the spectrum was recorded when the liquid was evaporated.

The in situ DRIFTS of nitrostyrene were recorded with a BRUKER Equinox 55 spectrometer equipped with a MCT detector in the range 800–2000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Before the test, the catalyst was packed into a sample cell with a ZnSe window. The background spectrum was recorded at 25 °C under atmospheric pressure in helium. Then, with the protection of pure helium, 5  $\mu$ l of 3-nitrostyrene was introduced into the sample for adsorption. Subsequently, 10 bar of hydrogen was introduced into the cell and the reaction temperature was increased to a fixed temperature with a heating rate of 15 °C/min. After obtaining the steady state, the spectra of 3-nitrostyrene hydrogenation process were collected at 50, 60, 70, 80, and 90 °C, respectively.

The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Au L<sub>III</sub> edge were recorded at the BL14W1 Shanghai Synchrotron Radiation Facility (SSRF) [32], Shanghai Institute of Applied Physics (SINAP), China. A double Si (1 1 1) crystal monochromator was used for the energy selection. The energy was calibrated by Au foil. The spectra were all collected at room temperature in the transmission mode. The data were analyzed by the Athena software package, with Artemis for fitting. The ranges used for data fitting in *k*-space and *R*-space were  $\Delta k$  3–12.5 Å<sup>-1</sup> and  $\Delta R$  1.2–3.3 Å, respectively.

### 3. Results and discussion

## 3.1. Catalytic performances

The distributions of the products with reaction time over the catalysts for the hydrogenation of 3-nitrostyrene (A) are shown in Fig. 1. One can see that the desired product, 3-vinylaniline (B), over the different catalysts increased linearly in the initial stage. Among them, the Au<sub>25</sub>/MgAl-HT-300 catalyst showed the lowest activity (Fig. 1a). Even when the reaction proceeded for 400 min, the 3-nitrostyrene still had not been converted completely, with a conversion of 88.2% and a selectivity of 96.3%. The Au<sub>25</sub>/ZnAl-HT-300 catalyst showed relatively moderate activity but the highest selectivity (Fig. 1b). After about 240 min, the 3-nitrostyrene was converted completely, and the selectivity of the 3-vinylaniline reached 99.3%. When the reaction time was prolonged

to 1000 min, the selectivity of 3-vinylaniline was maintained, with a trace of azo compound as the by-product. 3-Ethylaniline (D) was not detected, indicating that overhydrogenation of the substrate did not happen in this case, which agreed well with our previous work [28]. Over the Au<sub>25</sub>/NiAl-HT-300 catalyst (Fig. 1c), the nitro group was hydrogenated preferentially at the first stage. When the reaction proceeded for about 75 min, 3-ethylaniline appeared, indicating the hydrogenation of the C=C bond. After about 140 min, the desired product was almost completely overhydrogenated to 3-ethylaniline. The result suggested that the nitro group and the vinyl group might be competitively adsorbed on the Au<sub>25</sub>/NiAl-HT-300 catalyst, which behaved like the traditional gold systems (Au/ TiO<sub>2</sub> [9], Au/Al<sub>2</sub>O<sub>3</sub> [12], etc.). Over the three catalysts, 3ethylnitrobenzene (C) was not detected in the products, indicating that the vinyl group could not be preferentially hydrogenated. To sum up, the TOF values of the three catalysts were in the following sequence: Au<sub>25</sub>/MgAl-HT-300 < Au<sub>25</sub>/ZnAl-HT-300 < Au<sub>25</sub>/NiAl-HT-300, as listed in Table 1.

To confirm the different selectivity over the three catalysts, control experiments were conducted under the same reaction conditions to test the reactivity of the nitro group and the vinyl group using the styrene and the artificial mixture of nitrobenzene and styrene as substrates (Table 2). Only 2.0–5.5% of the styrene could be converted to ethylbenzene over the Au<sub>25</sub>/MgAl-HT-300 catalyst, which implied its low selectivity for the vinyl group. Over the Au<sub>25</sub>/ ZnAl-HT-300 catalyst, the styrene could hardly be converted, no matter if there was nitrobenzene in the substrate or not. However, the nitrobenzene and styrene could be completely converted over the Au<sub>25</sub>/NiAl-HT-300 catalyst. This indicated that the Au<sub>25</sub>/NiAl-HT-300 catalyst was highly active for the hydrogenation of both the nitro group and the vinyl group. The results agreed well with the kinetic data in Fig. 1.

## 3.2. Effect of particle sizes of Au

Well-defined layered structure characteristics of the supports and HT-supported Au<sub>25</sub> NCs were confirmed by XRD measurement, as shown in Fig. 2. Blank MgAl-HT, ZnAl-HT, and NiAl-HT (a, b, c) displayed patterns similar to those of the uncalcined samples



**Fig. 1.** The distributions of the products with reaction time for the hydrogenation of 3-nitrostyrene over the catalysts in the presence of H<sub>2</sub>: (a) Au<sub>25</sub>/MgAl-HT-300; (b) Au<sub>25</sub>/ ZnAl-HT-300; (c) Au<sub>25</sub>/NiAl-HT-300. Reaction conditions: 3-nitrostyrene: 0.4 mmol; catalyst: 50 mg; Au: ~0.63 mol%; H<sub>2</sub> pressure: 10 bar; reaction temperature: 90 °C.

Table 1
Catalytic results of the hydrogenation of 3-nitrostyrene over the supported gold catalysts.

Entry	Catalyst	Size (nm)	Time (h)	Conv. (%)	Sel. (%)	TOF $(h^{-1})^{a}$	TOF $(h^{-1})^{b}$
1	Au <sub>25</sub> /MgAl-HT-300	$2.2 \pm 0.8$	6.5	88.2	96.3	36.9	67.1
2	Au <sub>25</sub> /ZnAl-HT-300	$1.7 \pm 0.4$	4	96.9	99.3	71.1	101.6
3	Au25/NiAl-HT-300	$3.2 \pm 1.0$	1.25	95.0	96.9	133.4	351.1
4	Au/MgAl-HT-300	5.7 ± 12.9	16.5	3.0	>99	0.3	1.4
5	Au/ZnAl-HT-300	$2.6 \pm 0.8$	16.5	93.8	98.1	15.6	33.2
6	Au/NiAl-HT-300	$11.9 \pm 5.2$	16.5	69.4	9.5	9.0	74.8

*Note:* Reaction conditions: 3-nitrostyrene: 0.4 mmol; catalyst: 50 mg; Au: ~0.63 mol%; H<sub>2</sub> pressure: 10 bar; reaction temperature: 90 °C; solvent: 2 mL toluene. <sup>a</sup> The TOF was calculated based on the total loading of gold [10.28–30].

<sup>b</sup> The TOF was calculated based on the dispersion of gold [31].

Table 2

Control experiments over the three catalysts.

Entry	Catalysts	Conversion (%)		
		Styrene <sup>a</sup>	Styrene <sup>b</sup>	Nitrobenzene <sup>b</sup>
1	Au <sub>25</sub> /MgAl-HT-300	5.5	2.0	100
2	Au <sub>25</sub> /ZnAl-HT-300	1.0	0.9	100
3	Au <sub>25</sub> /NiAl-HT-300	100	100	100

Note: Reaction conditions: temperature 90 °C; H<sub>2</sub> pressure 10 bar; solvent 2 mL toluene; reaction time 4 h.

<sup>a</sup> Substrate: 0.4 mmol styrene.

<sup>b</sup> Substrate: 0.4 mmol styrene and 0.4 mmol nitrobenzene.

 $(a_1, b_1, c_1)$ : the obvious characteristic reflections of the layered structure with a series of narrow, symmetric, and strong peaks at low 2 $\theta$  angles (<25°) [33]. After calcination at 300 °C, the three catalysts  $(a_2, b_2, c_2)$  exhibited the patterns of the mixed oxide, which resembled those of MgO, ZnO, and NiO. Nevertheless, none of the diffraction peaks associated with Au were observed. This meant the gold NCs might be highly dispersed on the supports or the Au face-centered cubic structures could be covered by the diffraction peaks of the support.

To get the size distributions of the gold particles, we conducted HADDF-STEM characterization. From the images shown in Fig. 3, we can see that the average particle sizes of  $Au_{25}/MgAl-HT-300$ ,  $Au_{25}/ZnAl-HT-300$ , and  $Au_{25}/NiAl-HT-300$  catalysts were 2.2 ± 0.



Fig. 2. XRD patterns of (a) MgAl-HT; ( $a_1$ ) Au<sub>25</sub>/MgAl-HT; ( $a_2$ ) Au<sub>25</sub>/MgAl-HT-300; (b) ZnAl-HT; ( $b_1$ ) Au<sub>25</sub>/ZnAl-HT; ( $b_2$ ) Au<sub>25</sub>/ZnAl-HT-300; (c) NiAl-HT; ( $c_1$ ) Au<sub>25</sub>/NiAl-HT; ( $c_2$ ) Au<sub>25</sub>/NiAl-HT-300.

8 nm (Fig. 3a1),  $1.7 \pm 0.4$  nm (Fig. 3b1), and  $3.2 \pm 1.0$  nm (Fig. 3c1), respectively. Among them, the Au<sub>25</sub>/ZnAl-HT-300 catalyst showed the smallest average particle size and the narrowest size distribution. According to our previous work [28], the epitaxial interaction between the gold and the ZnAl-HT support and the formation of an Au–S–Zn bond might stabilize the gold particles. In this work, by the HRTEM characterization, the lattice matching between gold and the support were also found to exist in the Au<sub>25</sub>/MgAl-HT-300 (Fig. 3a2) and Au<sub>25</sub>/NiAl-HT-300 (Fig. 3c2) catalysts, which accorded with the previous work [33]. However, the size distributions of gold nanoparticles over these catalysts were different, which might be due to the different capability of the supports to stabilize gold NPs.

To illustrate the effect of particle sizes of Au on the selective hydrogenation of 3-nitrostyrene, we synthesized the corresponding gold catalysts over the three HT supports by deposition-precipi tation (DP), and denoted them as Au/MAI-HT-300. We calculated the average particle sizes of gold over these catalysts according to the HAADF-STEM images (Fig. S2). The average particle sizes of gold over Au/MgAl-HT-300, Au/NiAl-HT-300, and Au/ZnAl-HT-300 catalysts were 5.7 ± 12.9, 11.9 ± 5.2, and 2.6 ± 0.8 nm, respectively. They were larger than those of the corresponding  $Au_{25}/$ MAI-HT-300 catalysts. The size of the gold NPs depended on the nature of the support and the synthesis method. The residual sulfur of the thiolated Au<sub>25</sub> NCs was claimed to be critical for stabilizing the gold particles [28]. In the present work, according to the EDS mapping (Fig. S3) and EXAFS (Table S1 and Figs. S4 and S5) results, we demonstrated that residual sulfur still remained after calcination at 300 °C over the Au<sub>25</sub>/MAI-HT-300 samples, which might form the Au-S-M bonds and help to prevent the agglomeration of gold particles.

Thus, the catalytic performances were influenced accordingly. As shown in Table 1, the TOF values of the Au/MAI-HT-300 catalysts were much lower than those of the corresponding Au<sub>25</sub>/MAI-HT-300 catalysts, which are visualized in Fig. 4a. The reason that the Au/MAI-HT-300 catalysts were inferior to the Au<sub>25</sub>/MAI-HT-300 catalysts was the poor dispersion of gold on the samples obtained by the DP method. According to the plot of the TOF values with the average particle sizes of gold (Fig. 4b), the size of gold can influence the catalytic activity. The smaller particles rendered



Fig. 3. HAADF-STEM and HRTEM images of the Au<sub>25</sub>/MgAl-HT-300 (a<sub>1</sub>, a<sub>2</sub>), Au<sub>25</sub>/ZnAl-HT-300 (b<sub>1</sub>, b<sub>2</sub>), and Au<sub>25</sub>/NiAl-HT-300 (c<sub>1</sub>, c<sub>2</sub>) catalysts.



**Fig. 4.** The TOF values for hydrogenation of 3-nitrostyrene over different gold catalysts with respect to different supports (a) and the diameter of the gold particles (b). A and star mean catalysts prepared by impregnation (Au<sub>25</sub> as the precursor of the gold); B and ball mean catalysts prepared by DP.

higher activity than the bigger ones, in which the TOF values were improved exponentially with the decrease of the particle sizes of gold. Notably, the NiAl-HT- supported gold catalysts were beyond the law, because the Ni species probably promoted the dissociation of hydrogen [34–36]. The TOF values calculated by considering the dispersion of gold [30] were also plotted with the mean particle sizes of gold (Fig. S6), which displayed a tendency similar to that in Fig. 4.

# 3.3. Effect of the properties of the surfaces

Generally, the basicity of the catalysts could affect the reactivity for the hydrogenation of nitroaromatics [12,37]. Here, CO<sub>2</sub> TPD was

conducted to figure out the basicity of the supports and the corresponding Au catalysts. As shown in Fig. 5, the MgAl-HT-300 support and the Au<sub>25</sub>/MgAl-HT-300 catalyst displayed the strongest basicity: the amounts of basic sites calculated according to the desorbed CO<sub>2</sub> were 58.6 and 33.0  $\mu$ mol/g, respectively. They were followed by the NiAl-HT-300 support and the Au<sub>25</sub>/NiAl-HT-300 catalyst, where the amounts of basic sites decreased to 12.9 and 11.5  $\mu$ mol/g, respectively. The ZnAl-HT-300 (5.8  $\mu$ mol/g) support and the Au<sub>25</sub>/ZnAl-HT-300 (4.7  $\mu$ mol/g) showed the weakest basicity. According to the literature, the nitro group could be adsorbed easily on the basic surface [37,38]. The Au<sub>25</sub>/MgAl-HT-300 catalyst showed the lowest activity, although it exhibited the strongest basicity. Too strong basicity of the support (MgO, MgAl-HT, etc.)



**Fig. 5.**  $CO_2$  TPD spectra of the Au<sub>25</sub> NCs catalysts and the corresponding supports: (a) MgAl-HT-300; (b) Au<sub>25</sub>/MgAl-HT-300; (c) ZnAl-HT-300; (d) Au<sub>25</sub>/ZnAl-HT-300; (e) NiAl-HT-300; (f) Au<sub>25</sub>/NiAl-HT-300.

was detrimental to the hydrogenation of the nitro group, which has been verified by Shimizu et al. [12]. But the intrinsic reason was not clear. In our work, the  $Au_{25}/NiAl-HT-300$  catalyst with medium basicity showed the highest activity, which might be attributed to the easy activation of hydrogen over the Ni-based supports [34,35].

The in situ DRIFTS of CO adsorption was conducted to characterize the properties of the surfaces of the three catalysts. As shown in Fig. 6, the obvious band at around 2098 cm<sup>-1</sup> could be ascribed to the CO molecules adsorbed on metallic gold [39,40]. This was in good agreement with the results of XANES and EXAFS (Figs. S7, S8). However, one more band at 2048 cm<sup>-1</sup> appeared over the Au<sub>25</sub>/NiAl-HT-300 catalyst, which could be ascribed to CO adsorption on metallic nickel [41,42]. The reduction of the nickel in the support might be promoted by the gold, as manifested in the Au–Ni/SiO<sub>2</sub> bimetallic system [41]. The catalytic behavior of the Au<sub>25</sub>/NiAl-HT-300 catalyst was similar to that of the Au–Ni alloy catalysts, on which the vinyl group could be hydrogenated after the hydrogenation of the nitro group [43].

For most hydrogenation reactions over the supported gold catalysts, the activation and dissociation of hydrogen was the ratedetermining step [44–46]. In this work, to clarify the active site for hydrogen dissociation, blank experiments were conducted to evaluate the performance of the three supports. The results indicated that the supports themselves were not active for the hydrogenation of 3-nitrostyrene under the same reaction conditions as the catalysts, although they could adsorb the nitro groups of the substrates as well as the corresponding gold catalysts (Fig. S9). We can reasonably speculate that the gold on the surface of the catalysts played a key role in the dissociation of hydrogen. The activation of hydrogen on the gold surfaces was investigated by Corma's group by density functional theory (DFT) calculations [13]. They discovered that the gold atoms active for H<sub>2</sub> dissociation were neutral or had a net charge close to zero. Here, we found there was metallic gold on the surfaces of the three catalysts, which acted as the active site for the activation of hydrogen. The high selectivity for the hydrogenation of the -NO<sub>2</sub> over the three catalysts at the beginning stage was attributed to the metallic gold. However, the metallic nickel on the surface of the Au<sub>25</sub>/NiAl-HT-300 catalyst could help to activate hydrogen and lead to the hydrogenation of the vinyl bond after the nitro group was hydrogenated.

#### 3.4. Reaction route

The generally accepted reaction mechanism for the hydrogenation of aromatic nitro compounds was divided into the direct route and the condensation route [47]. Aniline derivatives were reported to form on the Pt/CaCO<sub>3</sub> or Pt/C–H<sub>3</sub>PO<sub>4</sub> catalysts through both routes, whereas on the Au/TiO<sub>2</sub> catalyst, the reduction of aromatic nitro compounds did not follow the condensation route but only the direct route [48]. In this work, the azo compounds were detected during the catalytic processes of the three catalysts



Fig. 6. In situ CO-DRIFTS spectra of adsorbed CO over Au NCs catalysts: (a) Au<sub>25</sub>/MgAl-HT-300; (b) Au<sub>25</sub>/ZnAl-HT-300; (c). Au<sub>25</sub>/NiAl-HT-300.



Fig. 7. In situ DRIFTS spectra of adsorbed nitrostyrene over the catalysts: (a)  $Au_{25}/MgAl-HT-300$ ; (b)  $Au_{25}/ZnAl-HT-300$ ; (c)  $Au_{25}/NiAl-HT-300$  at 25 °C (1), 50 °C (2), 60 °C (3), 70 °C (4), 80 °C (5), and 90 °C (6) before (1) and after (2–6) introduction of 10 bar of H<sub>2</sub>.



**Scheme 1.** Proposed reaction mechanism for the hydrogenation of 3-nitrostyrene over the three catalysts.

(Fig. S9), suggesting that they were following the condensation route to produce 3-vinylaniline. To further investigate the reaction path of the hydrogenation processes over the three catalysts, we employed in situ DRIFTS under 10 bar of hydrogen to detect the intermediate products. The adsorption spectra are displayed in Fig. 7. Before the hydrogen was introduced, the bands at 1540 and 1358 cm<sup>-1</sup> due to the  $v_{as}(NO_2)$  and  $v_s(NO_2)$  of the adsorbed nitro species [12,49] and the band at 1633 cm<sup>-1</sup> due to the v (C=C) [9] were observed over the three catalysts. When the pressure of the hydrogen was enhanced to 10 bar, the IR band at 1558 cm<sup>-1</sup> appeared on all of the catalysts with increasing temperature, which could be assigned to the vibrations of the N=N bond [50]. This agreed well with the results of chromatographic analysis (Fig. S10). That meant that the reduction of nitrostyrene on the Au<sub>25</sub>/MAI-HT-300 catalysts followed the condensation route. The bands at 1620, 1604, and 1493 cm<sup>-1</sup> were ascribed to aniline [12,51], which was produced during the hydrogenation of the substrate. The intensity of these bands appeared much higher over the Au<sub>25</sub>/NiAl-HT-300 than on the other two catalysts. This suggested that the Au<sub>25</sub>/NiAl-HT-300 catalyst exhibited the highest catalytic activity, in accordance with the reactivity evaluation results. The new bands at 1583 cm<sup>-1</sup> (-NO) [52,53] and 1462 cm<sup>-1</sup> (-NOH) [49] were observed on the  $Au_{25}/NiAl-HT-300$  catalyst but not on the Au<sub>25</sub>/MgAl-HT-300 and Au<sub>25</sub>/ZnAl-HT-300 samples. This

implied that the reaction path on the  $Au_{25}$ /NiAl-HT-300 catalyst also followed the direct route as well as the condensation route.

Based on the above results and our kinetic data over the three catalysts, we propose a reaction pathway for the hydrogenation of 3-nitrostyrene over the three catalysts (Scheme 1). There was a condensation route over the three catalysts: The 3-nitrostyrene was first reduced to the nitroso compound and then to the hydroxylamine compound, followed by one molecule of the nitroso compound and a molecule of the hydroxylamine producing one molecule of the azo compound, which was consecutively reduced to the hydrazo and aniline compounds. As indicated by the in situ DRIFTS results in Fig. 7, there was also a direct route over the Au<sub>25</sub>/NiAl-HT-300 catalyst, which permitted direct transformation from nitrostyrene to aniline compounds. Furthermore, overhydrogenation to aminoethylbenzene could also happen over the Au<sub>25</sub>/NiAl-HT-300 catalyst. The difference in reaction pathways of Au<sub>25</sub>/NiAl-HT-300 from those of the others might be caused by the appearance of the metallic nickel, which could enhance the reactivity and influence the selectivity.

## 4. Conclusions

The effect of the divalent metal ions in the hydrotalcite on the catalytic performance of the Au<sub>25</sub>/MAI-HT-300 catalyst for the hydrogenation of 3-nitrostyrene was investigated. The three catalysts exhibited different catalytic performance. The highest TOF was obtained over the Au<sub>25</sub>/NiAl-HT-300 catalyst, but severe overhydrogenation to 3-ethylaniline was observed with prolonged reaction time. Inferior activity was obtained over the Au<sub>25</sub>/ZnAl-HT-300 and Au<sub>25</sub>/MgAl-HT-300 catalysts. The selectivity for the desired product was highest over the Au<sub>25</sub>/ZnAl-HT-300 catalyst, on which the selectivity of 3-vinylstyrene could be maintained at above 98% even after the nitro group of the substrate was converted completely. When CO was used as the probe molecule, the in situ DRIFTS results showed that the gold in a metallic state over the three catalysts led to superior hydrogenation of the nitro group. Meanwhile, the new absorption band at 2048 cm<sup>-1</sup> due to the metallic Ni over the Au<sub>25</sub>/NiAl-HT-300 catalyst indicated that Ni intimately interacted with Au could be reduced at room temperature, which contributed to the high reactivity and overhydrogenation. Based on the in situ DRIFTS results of 3-nitrostyene adsorption at 10 bar of hydrogen, the three catalysts all followed the condensation route, while the direct route only appeared on the Au<sub>25</sub>/NiAl-HT-300 catalyst. Accordingly, the effect of the divalent metal ions on the reaction pathways of the Au<sub>25</sub>/MAI-HT-300 catalysts for the selective hydrogenation of the 3-nitrostyrene was clearly pictured. This study will provide a good reference for the design of gold catalysts with high chemoselectivity for fine chemical synthesis.

#### Notes

The authors declare no competing financial interest.

# Supporting information

UV-visible spectra of the thiolated  $Au_{25}$  NCs, XANES and EXAFS results of the three catalysts, HAADF-STEM images of the gold catalysts prepared by the DP method, the ATR-FTIR spectra of the 3-nitrostyrene on the three catalysts and supports, and some other results are available free of charge at http://pubs.acs.org.

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