



# 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

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 (~2.7 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 3-nitrostyrene using ZnAl-HT supported thiolated Au<sub>25</sub> NCs as a precatalyst [28]. We found that, unlike other gold catalysts [9,12]. The

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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 hydroxalcalcites (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<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub> 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<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.21 mol) and Al(NO<sub>3</sub>)<sub>3</sub>·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 hydroxalcalcite 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 3-nitrostyrene 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

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