

Article

Selective Hydrogenation of Cinnamaldehyde Catalyzed by ZnO-Fe₂O₃ Mixed Oxide Supported Gold Nanocatalysts

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Abstract: ZnO-Fe₂O₃ mixed oxides and supported gold nanocatalysts were prepared by using coprecipitation and deposition–precipitation methods, respectively. Cinnamaldehyde hydrogenation over various ZnO-Fe₂O₃ mixed oxides supported gold nanocatalysts have been investigated at 140 °C and a hydrogen pressure of 1.0 MPa. The molar ratio of Fe to Zn was found to greatly affect the selective hydrogenation catalytic activity of ZnO-Fe₂O₃ mixed oxide supported gold nanocatalysts. Among these supported gold nanocatalysts in this work, Au/Zn_{0.7}Fe_{0.3}O_x (Au loading of 1.74 wt %) exhibited the highest conversion of cinnamaldehyde and high selectivity to cinnamal alcohol. The excellent catalytic activity of Au/Zn_{0.7}Fe_{0.3}O_x was tightly associated with a large surface area, small gold nanoparticles, and good H₂ dissociation ability at low temperature.

Keywords: gold catalysis; zinc-iron mixed oxides; selective hydrogenation; cinnamaldehyde; cinnamyl alcohol

1. Introduction

Unsaturated alcohols are valuable chemical intermediates and widely used in pharmaceuticals, perfumes, and flavors [1,2]. Selective hydrogenation of α,β -unsaturated aldehydes to the corresponding unsaturated alcohols is a scientific challenge in heterogeneous catalysis because hydrogenation of the conjugated C=C bond is thermodynamic and kinetically favored, in comparison to that of the C=O group [3,4]. For the selective hydrogenation of cinnamaldehyde, a typical α,β -unsaturated aldehyde, the realization of efficient hydrogenation of the C=O group without hydrogenation of the conjugated C=C bond is of great research interest and industrial importance [5,6].

Although gold was regarded as a poor catalyst for a long time, gold nanoparticles (NPs) highly dispersed on metal oxides were very active for many reactions, such as CO oxidation [7] and propylene epoxidation [8]. Most research work on noble metal nanocatalysts, especially for gold nanocatalyst, has been focused on oxidation reactions [9,10], and more extensive studies on highly efficient hydrogenations are required [11–15]. In the selective hydrogenation of unsaturated α,β -aldehydes, gold nanocatalysts have shown high selectivity toward the C=O group hydrogenation to the unsaturated alcohol, while other noble metals like Pd and Pt often present intrinsic selectivity toward C=C bond hydrogenation to saturated aldehyde [16]. For example, Hutchings et al. found that

Au/ZnO catalyzed selective hydrogenation of but-2-enal to but-2-en-1-ol with the selectivity of 80% [17]. Jin et al. observed that atomically precise $\text{Au}_{25}(\text{SR})_{18}$ clusters supported on Fe_2O_3 and TiO_2 catalyzed the selective hydrogenation of α,β -unsaturated carbonyl compounds to unsaturated alcohols through the coordination of C=O group to the “hole” site of Au clusters [18]. Cao et al. reported that gold NPs supported on mesostructured CeO_2 efficiently catalyzed selective hydrogenation of a range of α,β -unsaturated carbonyl compounds to unsaturated alcohols in neat water [19]. Claus et al. identified the edges of gold NPs supported on ZnO as the active sites of the Au/ZnO catalyst for the preferential hydrogenation of C=O group of acrolein to allyl alcohol [20]. Li et al. reported that Au/ TiO_2 catalyzed the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol with a selectivity of 83% and the doping of Au/ TiO_2 by Ir improved the conversion of cinnamaldehyde without the loss of selectivity to cinnamyl alcohol [21].

Concerning the selective hydrogenation of cinnamaldehyde over Au/ZnO nanocatalyst, Larese and co-researchers have investigated three different Au/ZnO nanocatalysts—including Au/rod-tetrapod ZnO, Au/porous ZnO, and Au/ZnO-CP—and found that Au/ZnO-CP prepared by a method of coprecipitation (CP) exhibited excellent activity with cinnamaldehyde conversion of 94.9% and cinnamal alcohol selectivity of 100% [13]. Our group previously investigated the catalytic properties of Au NPs supported on various metal oxides for the selective hydrogenation of cinnamaldehyde, and found that Au/ZnO nanocatalyst exhibited the highest selectivity to cinnamyl alcohol of 86% [22]. However, the catalytic performance of Au/ZnO was relatively low, especially at low reaction temperature. After reaction at 150 °C for 18 h, Au/ZnO gave a low conversion of cinnamaldehyde (23%). The different activity of Au/ZnO nanocatalyst in the above literature and in our work might be caused by some factors such as different reaction conditions and different preparation method of gold nanocatalysts. To further improve the catalytic performance of Au/ZnO, we herein utilized ZnO- Fe_2O_3 mixed oxides instead of ZnO to support Au NPs for the selective hydrogenation of cinnamaldehyde. The results showed that Au/ $\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$ with a Au loading of 1.74 wt %, markedly enhanced the conversion of cinnamaldehyde, exhibiting the highest conversion of cinnamaldehyde of 75.4% after reaction at 140 °C for 10 h, and at same time achieving high selectivity of cinnamyl alcohol (88.5%).

2. Results and Discussion

Figure 1a shows the X-ray powder diffraction (XRD) patterns of ZnO, ZnO- Fe_2O_3 mixed oxides, and Fe_2O_3 supports. The diffraction peaks at $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.4^\circ, 56.6^\circ, 62.8^\circ$, and 68° were assigned to ZnO (JCPDS PDF# 79-2205). The diffraction at $2\theta = 24.1^\circ, 33.1^\circ, 35.6^\circ, 40.9^\circ, 49.4^\circ, 54.0^\circ, 62.4^\circ$, and 64.0° were attributed to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS PDF# 86-2368). With the increase of the content of iron, the intensity of diffraction peaks of ZnO were gradually decreased in XRD pattern of ZnO- Fe_2O_3 mixed oxide. For the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}_x$ and $\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$ mixed oxides, there was not any diffraction of iron oxides, but only peaks due to ZnO were observed. For the $\text{Zn}_{0.5}\text{Fe}_{0.5}\text{O}_x$ and $\text{Zn}_{0.3}\text{Fe}_{0.7}\text{O}_x$ mixed oxides, diffraction peaks at $2\theta = 29.9^\circ, 35.1^\circ$, and 42.7° appeared, which could be assigned to ZnFe_2O_4 (JCPDS PDF# 74-2397), indicating that phase separation occurred. For $\text{Zn}_{0.1}\text{Fe}_{0.9}\text{O}_x$ mixed oxide, only small diffraction signals of Fe_2O_3 were observed, suggesting the crystal particles of iron oxide were very small. Figure 1b shows the XRD patterns of the supported gold nanocatalysts. The loading of gold did not result in an obvious change in the crystal structure of the corresponding support. No diffraction signals of gold were detected, due to the low gold loading and good dispersion of Au NPs [23].

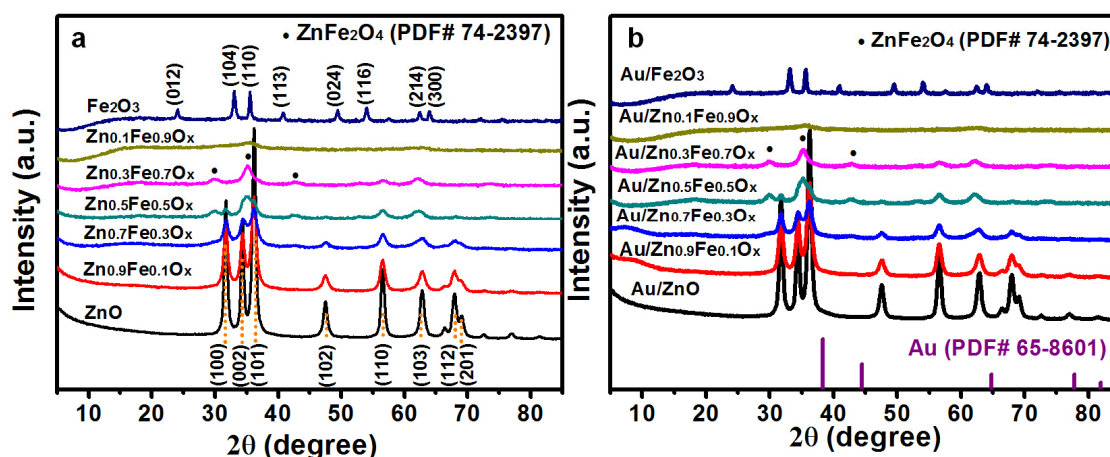


Figure 1. XRD pattern of (a) supports and (b) supported gold nanocatalysts.

The reduction behavior of the as-prepared supports and supported gold nanocatalysts was examined by hydrogen temperature programmed reduction (H₂-TPR). As shown in Figure 2A, ZnO did not present reduction peaks, which was probably the result of complete dihydroxylation and high thermal stability [24,25]. There were three reduction peaks for the Fe₂O₃: the first reduction peak below 400 °C was due to the reduction of Fe₂O₃ to Fe₃O₄, while the broad peaks above 400 °C represented the further reduction of Fe₃O₄ to metallic iron, perhaps through FeO [26,27]. All the mixed oxides showed different reduction behavior. Figure 2B shows the H₂-TPR profiles of the supported gold nanocatalyst. With the loading of Au NPs, the reduction peaks shifted to lower temperatures. For Au/Zn_{0.7}Fe_{0.3}O_x, Au/Zn_{0.3}Fe_{0.7}O_x, and Au/Fe₂O₃, there were low temperature reduction peaks around 120 °C, which were attributed to the reduction of gold species [28]. For Au/Zn_{0.1}Fe_{0.9}O_x, there was a relatively stronger reduction peak around 120 °C, which could be due to reduction of gold species and partial reduction of Fe₂O₃ to Fe₃O₄. For Au/Zn_{0.9}Fe_{0.1}O_x and Au/Zn_{0.5}Fe_{0.5}O_x, there were almost no reduction peaks at low temperature around 120 °C in the inset of Figure 2B. For Au/Zn_{0.9}Fe_{0.1}O_x, the reduction peak center at 640 °C shifted to 490 °C, indicating there also exist interaction between gold and iron oxide in the support. The absence of low temperature reduction peak around 120 °C for Au/Zn_{0.9}Fe_{0.1}O_x is due to low iron content in the support. There was a small change on reduction peaks between Zn_{0.5}Fe_{0.5}O_x and Au/Zn_{0.5}Fe_{0.5}O_x, indicating the weak interaction between gold and support. The shift of reduction peaks to lower temperature could be due to many factors, such as reduction of gold species, a gold-catalyzed hydrogenation reaction, and other combined effects [29,30]. The hydrogen dissociation ability of gold catalyst is one of factors resulting in peak shifts. Based on the data from XRD pattern, it exhibited that Zn_{0.5}Fe_{0.5}O_x possessed two phases including ZnO and ZnFe₂O₄. In this work, we found that Au/Zn_{0.5}Fe_{0.5}O_x, containing Au/ZnO and Au/ZnFe₂O₄, displayed lower cinnamaldehyde (CAL) conversion and higher cinnamyl alcohol (COL) selectivity than Au/ZnO and Au/Fe₂O₃ (Table 4). Sakurai et al. used Au/ZnO, Au/Fe₂O₃, and Au/ZnFe₂O₄ to catalyzed CO₂ hydrogenation and found that Au/ZnFe₂O₄ showed much lower CO₂ conversion and higher methanol selectivity than Au/ZnO and Au/Fe₂O₃ at the reaction temperature of 250 °C [31]. In other words, Au/ZnFe₂O₄ possessed lower hydrogen dissociation ability than Au/ZnO and Au/Fe₂O₃. The results in this work are consistent with the work reported by Sakurai and co-workers. The poor hydrogen dissociation ability of Au/Zn_{0.5}Fe_{0.5}O_x may be the reason why there was no reduction peak around 120 °C. The Fe/Zn molar ratio of Zn_{0.3}Fe_{0.7}O_x was 7/3, indicating there were three crystal phases (ZnO, ZnFe₂O₄, Fe₂O₃) in Zn_{0.3}Fe_{0.7}O_x. However, the Fe₂O₃ phase was not detected by XRD diffraction owing to the small crystal particles. The presence of low temperature reduction peak around 120 °C for Au/Zn_{0.3}Fe_{0.7}O_x is due to the formation of Fe₂O₃ phase. The H₂ consumption amount in TPR was summarized in Table 1. It was noted that the H₂ consumption amount almost monotonously increased with the increasing of the theoretical addition of Fe in the supports.

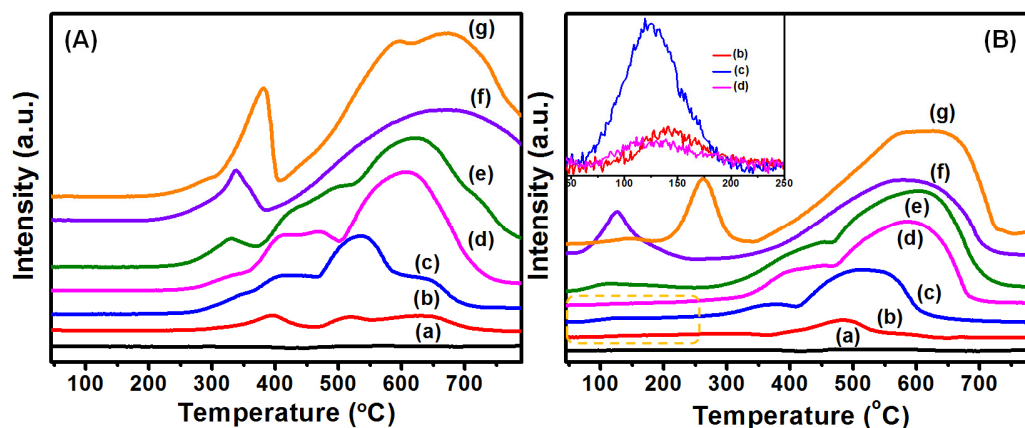


Figure 2. (A) H₂-TPR profiles of (a) ZnO, (b) Zn_{0.9}Fe_{0.1}O_x, (c) Zn_{0.7}Fe_{0.3}O_x, (d) Zn_{0.5}Fe_{0.5}O_x, (e) Zn_{0.3}Fe_{0.7}O_x, (f) Zn_{0.1}Fe_{0.9}O_x, and (g) Fe₂O₃; (B) H₂-TPR profiles of (a) Au/ZnO, (b) Au/Zn_{0.9}Fe_{0.1}O_x, (c) Au/Zn_{0.7}Fe_{0.3}O_x, (d) Au/Zn_{0.5}Fe_{0.5}O_x, (e) Au/Zn_{0.3}Fe_{0.7}O_x, (f) Au/Zn_{0.1}Fe_{0.9}O_x, and (g) Au/Fe₂O₃. The enlarged H₂-TPR profiles of (b) Au/Zn_{0.9}Fe_{0.1}O_x, (c) Au/Zn_{0.7}Fe_{0.3}O_x, (d) Au/Zn_{0.5}Fe_{0.5}O_x from 50 to 250 °C subtracted the baseline in the inset of Figure 2B.

Table 1. H₂ consumption amount in TPR experiments from 50 to 800 °C.

Support	H ₂ Consumption (μmol/g)	Catalyst	H ₂ Consumption (μmol/g)
ZnO	0	Au/ZnO	0
Zn _{0.9} Fe _{0.1} O _x	790	Au/Zn _{0.9} Fe _{0.1} O _x	719
Zn _{0.7} Fe _{0.3} O _x	3041	Au/Zn _{0.7} Fe _{0.3} O _x	2750
Zn _{0.5} Fe _{0.5} O _x	4913	Au/Zn _{0.5} Fe _{0.5} O _x	4901
Zn _{0.3} Fe _{0.7} O _x	7095	Au/Zn _{0.3} Fe _{0.7} O _x	6413
Zn _{0.1} Fe _{0.9} O _x	6623	Au/Zn _{0.1} Fe _{0.9} O _x	5444
Fe ₂ O ₃	9327	Au/Fe ₂ O ₃	7839

Table 2 summarizes Brunner–Emmet–Teller (BET) surface areas, pore volumes, and average pore diameters of supported gold nanocatalysts. It can be seen that the surface areas of the Au/ZnO (62.6 m²/g) and Au/Fe₂O₃ (82 m²/g) are smaller than those of Au/mixed oxides (122–148 m²/g) except for Au/Zn_{0.9}Fe_{0.1}O_x. It is worth noting that the doping of iron into ZnO affects the physical properties of the oxides. With the increase of iron content in the mixed oxide, BET surface areas increase, but pore volumes and average pore diameters decrease. As also shown in Table 2, the actual gold loading of the five types of nanocatalysts (1.60–1.74 wt %), determined by inductively coupled plasma optical emission spectrometry (ICP-OES) measurement, were close to the target value of 2 wt %, suggesting that there was no substantial escape of gold during deposition–precipitation. The actual gold loadings of Au/mixed oxides are slightly higher than those of Au/ZnO and Au/Fe₂O₃.

Table 2. BET surface area, pore volume, average pore diameter, and actual gold loading of the supported gold nanocatalysts.

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Au Loading ^a (wt %)
Au/ZnO	62.6	0.47	30.2	1.65
Au/Zn _{0.9} Fe _{0.1} O _x	72.3	0.38	20.8	-
Au/Zn _{0.7} Fe _{0.3} O _x	136.5	0.36	10.5	1.74
Au/Zn _{0.5} Fe _{0.5} O _x	122.6	0.22	7.1	1.70
Au/Zn _{0.3} Fe _{0.7} O _x	141.4	0.17	4.7	1.74
Au/Zn _{0.1} Fe _{0.9} O _x	148.2	0.19	5.0	-
Au/Fe ₂ O ₃	82.0	0.17	8.5	1.60

^a Data determined by ICP-OES technology. - Data was not determined.

Figure 3 shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the supported gold nanocatalysts prepared by DP method. It can be clearly seen that the gold NPs were homogeneously dispersed on the surface of $\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$, while the gold NPs were less uniformly dispersed on the surface of ZnO , $\text{Zn}_{0.5}\text{Fe}_{0.5}\text{O}_x$, $\text{Zn}_{0.3}\text{Fe}_{0.7}\text{O}_x$, and Fe_2O_3 . On $\text{Au}/\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$, many small Au clusters (<2.0 nm) could be clearly observed. Figure 4 shows the distributions of gold particles diameter of supported gold nanocatalysts prepared by DP method. For $\text{Au}/\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$, the diameter distribution of gold particles was very narrow (0.5–4.5 nm), giving a mean diameter of 2.0 nm, and about 50% of Au particles were clusters (<2.0 nm). In contrast, for Au/ZnO , $\text{Au}/\text{Zn}_{0.5}\text{Fe}_{0.5}\text{O}_x$, and $\text{Au}/\text{Zn}_{0.3}\text{Fe}_{0.7}\text{O}_x$, the diameter distributions of Au particles were relatively broad (1.0–7.5 nm), and less than 7% of Au particles existed as clusters (<2.0 nm), leading to relatively larger mean diameter (3.3, 3.2, and 3.3 nm respectively). In addition, for $\text{Au}/\text{Fe}_2\text{O}_3$, the diameter distributions of Au particles were very broad (1.0–10.0 nm), giving larger mean diameter (3.9 nm), and less than 3% of Au particles were clusters (<2.0 nm). After all, the diameter distribution of gold particles of $\text{Au}/\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$ was the narrowest and the mean diameter (2.0 nm) was the smallest.

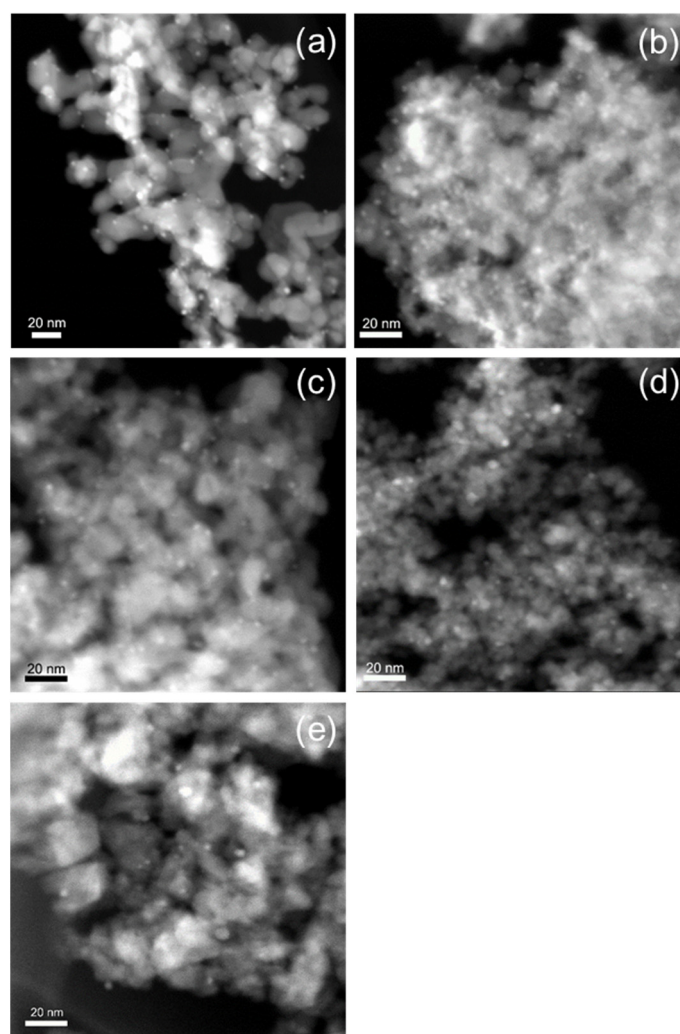


Figure 3. HAADF-STEM images of (a) Au/ZnO , (b) $\text{Au}/\text{Zn}_{0.7}\text{Fe}_{0.3}\text{O}_x$, (c) $\text{Au}/\text{Zn}_{0.5}\text{Fe}_{0.5}\text{O}_x$, (d) $\text{Au}/\text{Zn}_{0.3}\text{Fe}_{0.7}\text{O}_x$, and (e) $\text{Au}/\text{Fe}_2\text{O}_3$.

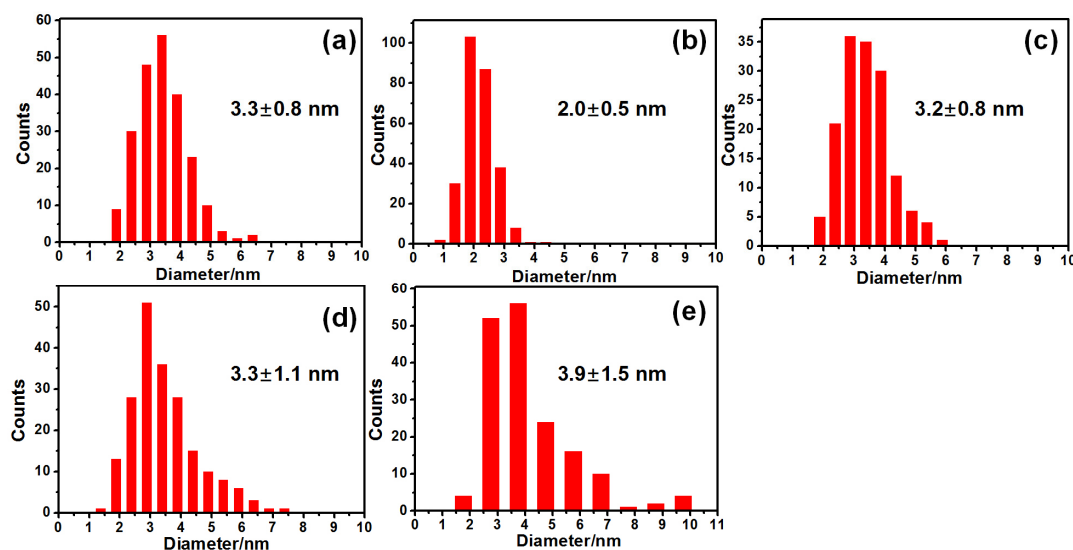


Figure 4. Au particle size distributions of (a) Au/ZnO, (b) Au/Zn_{0.7}Fe_{0.3}O_x, (c) Au/Zn_{0.5}Fe_{0.5}O_x, (d) Au/Zn_{0.3}Fe_{0.7}O_x, and (e) Au/Fe₂O₃.

Additional characterization by X-ray photoelectron spectroscopy (XPS) was carried out on selected nanocatalysts of Au/ZnO, Au/Zn_{0.7}Fe_{0.3}O_x, Au/Zn_{0.5}Fe_{0.5}O_x, and Au/Fe₂O₃. The Au 4f region of samples in Figure 5 and Table 3 displayed the valuable information at the binding energy of 83.19–83.47 eV, indicating a negative shift of 0.53–0.81 eV relative to 84.0 eV of bulk Au [32,33]. This result might cause by electron transfer from the support to Au due to the strong electronic interaction between Au nanoparticles and support [34,35]. It was noted that the Au 4f_{5/2} and 4f_{7/2} clearly indicated that the major gold species on the selected catalysts was metallic gold. It was known that there might be partially charged Au at the perimeter interfaces due to the strong interaction between Au and supports. However, in this work the Zn 3p_{3/2} and Zn 3p_{1/2} peaks overlapped with the signals of Au (I) 4f_{5/2} and Au (III) 4f_{5/2}, respectively. Therefore, only Au (0) species in the samples could be clear confirmed. Based on the Zn 2p and Fe 2p summarized in Table 3, the existence of Zn²⁺ and Fe³⁺ could be observed as ZnFe₂O₄ [36,37].

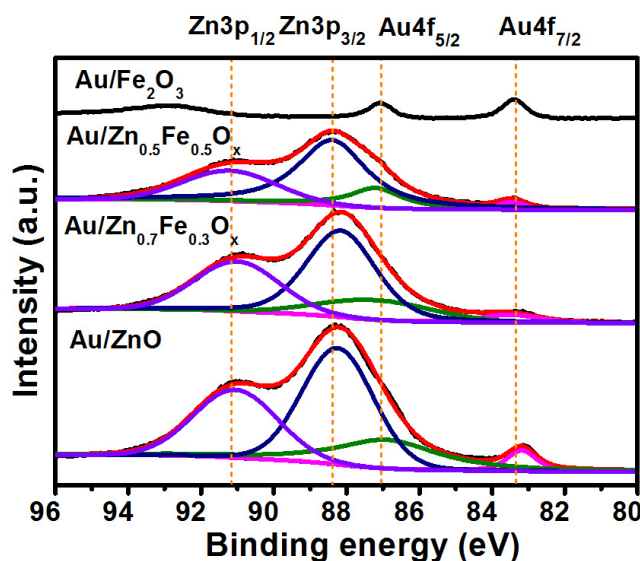


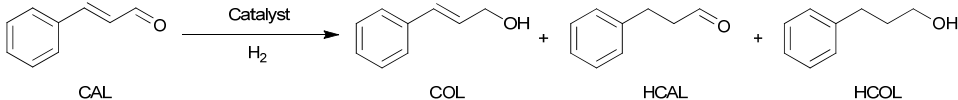
Figure 5. XPS spectra of Au 4f region in the selected nanocatalysts of Au/ZnO, Au/Zn_{0.7}Fe_{0.3}O_x, Au/Zn_{0.5}Fe_{0.5}O_x, and Au/Fe₂O₃.

Table 3. Data from the XPS analyses of the selected nanocatalysts.

Catalyst	Au4f _{7/2} (eV)	Au4f _{5/2} (eV)	Zn3p _{3/2} (eV)	Zn3p _{1/2} (eV)	Zn2p _{3/2} (eV)	Zn2p _{1/2} (eV)	Fe2p _{3/2} (eV)	Fe2p _{1/2} (eV)
Au/ZnO	83.19	86.89	88.24	91.04	1021.30	1044.35	-	-
Au/Zn _{0.7} Fe _{0.3} O _x	83.50	87.20	88.16	91.01	1021.00	1044.20	710.30	724.20
Au/Zn _{0.5} Fe _{0.5} O _x	83.46	87.20	88.40	91.20	1021.50	1044.75	711.00	724.50
Au/Fe ₂ O ₃	83.47	87.13	-	-	-	-	710.38	723.70

Table 4 summarizes the reaction results of Au NPs supported on ZnO-Fe₂O₃ metal oxides in selective hydrogenation of cinnamaldehyde at 140 °C under 1.0 MPa of H₂. Au/ZnO showed very high cinnamyl alcohol selectivity (90.7%), but low cinnamaldehyde conversion (30.2%). In contrast, various ZnO-Fe₂O₃ mixed oxide supported gold nanocatalysts showed differing activity and selectivity toward COL depending on the molar ratio of Fe to Zn in the mixed oxides. When the Fe/Zn molar ratio was increased from 1/9 to 3/7, the conversion of CAL was significantly increased, with a slight decrease of COL selectivity. As the molar ratio of Fe/Zn increased to 5/5, the highest COL selectivity (93.0%) and lowest CAL conversion (18.3%) were achieved. Upon a further increase of the Fe/Zn ratio from 7/3 to 9/1, the catalytic performance became similar to that of Au/Fe₂O₃. Interestingly, the molar ratio of Fe to Zn was found to greatly affect the catalytic activity of ZnO-Fe₂O₃ mixed oxide supported gold nanocatalysts. Among all the gold nanocatalysts in this work, Au/Zn_{0.7}Fe_{0.3}O_x exhibited the highest conversion of CAL (75.4%) and high selectivity to COL (88.5%).

Table 4. Selective hydrogenation of cinnamaldehyde over the supported gold nanocatalysts.

					
Catalyst	Conversion (%)	Selectivity (%)			COL Yield (%)
		COL	HCAL	HCOL	
Au/ZnO	30.2	90.7	7.0	2.3	27.4
Au/Zn _{0.9} Fe _{0.1} O _x	50.6	86.8	9.0	4.2	43.9
Au/Zn _{0.7} Fe _{0.3} O _x	75.4	88.5	4.0	7.5	66.7
Au/Zn _{0.5} Fe _{0.5} O _x	18.3	93.0	5.9	1.1	17.0
Au/Zn _{0.3} Fe _{0.7} O _x	55.6	88.9	5.1	6.0	49.4
Au/Zn _{0.1} Fe _{0.9} O _x	50.4	85.4	8.0	6.6	43.0
Au/Fe ₂ O ₃	57.0	80.2	12.3	7.5	45.7

Reaction condition: catalyst (60 mg, Au: 0.32 mol %), CAL (1.6 mmol), nonane (0.8 mmol), isopropyl alcohol (15 mL), temperature (140 °C), H₂ (1.0 MPa), reaction time (10 h). The conversion and selectivity were determined by GC analysis with nonane as an internal standard.

Furthermore, non-polar (toluene) and polar (ethanol, isopropanol) solvents were chosen to study solvent effect on hydrogenation catalytic activity of the Au/Zn_{0.7}Fe_{0.3}O_x catalyst. It was found that the nature of solvent had a great influence on both CAL conversion and COL selectivity in Table 5. CAL conversion was very low when using toluene as solvent. The CAL conversion was much higher in isopropanol and ethanol than that in toluene. However, a large amount of undesired products was detected when using ethanol as solvent. The result in this work was consistent with the work of Srinivas and co-workers [38]. The effect of hydrogen pressure on CAL hydrogenation over the Au/Zn_{0.7}Fe_{0.3}O_x catalyst was also investigated. When hydrogen pressure was increased from 1.0 to 2.0 MPa, a decrease of COL selectivity was observed with slight increase in CAL conversion (Table 5). High hydrogen pressure could improve the solubility of hydrogen, thus improving the CAL conversion, but it was also benefit for C=C hydrogenation.

Table 5. Effect of solvent and hydrogen pressure on the hydrogenation of cinnamaldehyde over Au/Zn_{0.7}Fe_{0.3}O_x.

Solvent	H ₂ Pressure (MPa)	Conversion (%)	Selectivity (%)			
			COL	HCOL	HCOL	Others
Toluene	1.0	1.0	89.3	10.7	0.0	0.0
Ethanol	1.0	70.2	57.9	9.8	1.0	31.3
Isopropanol	1.0	75.4	88.5	4.0	7.5	0.0
Isopropanol	2.0	78.3	86.1	6.3	7.6	0.0

Reaction condition: catalyst (60 mg, Au: 0.32 mol %), CAL (1.6 mmol), nonane (0.8 mmol), solvent (15 mL), temperature (140 °C, reaction time (10 h). The conversion and selectivity were determined by GC analysis with nonane as an internal standard.

Substrate conversion and target product selectivity in the selective hydrogenation of α,β -unsaturated aldehyde were often found to be sensitive to the reaction temperature [39–41]. Table 6 shows the effect of reaction temperature (80–140 °C) on catalytic performance of Au/ZnO, Au/Fe₂O₃, Au/Zn_{0.7}Fe_{0.3}O_x, and Au/Zn_{0.5}Fe_{0.5}O_x nanocatalysts in the selective hydrogenation of cinnamaldehyde. Au/Zn_{0.7}Fe_{0.3}O_x and Au/Fe₂O₃ showed low conversion (<5%) with high COL selectivity at 80 °C, while Au/ZnO and Au/Zn_{0.5}Fe_{0.5}O_x were inactive under the same condition. Au/ZnO showed very low conversion (<5%) with high COL selectivity (>90%) at 100 °C and 120 °C, indicating that Au/ZnO needed higher temperature to initiate cinnamaldehyde hydrogenation. Au/Zn_{0.5}Fe_{0.5}O_x exhibited very low conversion at 80 to 140 °C, probably due to the weak interaction between Au and Zn_{0.5}Fe_{0.5}O_x support. As the reaction temperature was raised from 100 to 140 °C, the CAL conversion of Au/Zn_{0.7}Fe_{0.3}O_x increased continuously from 12.3 to 75.4%, along with a slight decrease of COL selectivity from 91.3 to 88.5%, due to a little deep hydrogenation of COL to HCOL at high reaction temperatures. Obviously, Au/Zn_{0.7}Fe_{0.3}O_x catalyst showed higher CAL conversion and higher COL selectivity than Au/Fe₂O₃ at all temperatures. For further comparison, the reported data by other groups were listed in the Table 7. It was clear that Au/ZnO prepared by CP method (Au/ZnO-CP) in literature exhibited both the highest hydrogenation conversion of CAL (94.9%) and selectivity of COL (100%) [13]. In our work, Au/ZnO prepared using DP method displayed high selectivity of COL (90.7%) but low conversion of CAL (30.2%). When Zn_{0.7}Fe_{0.3}O_x was used to support gold NPs, CAL conversion was greatly enhanced, and COL selectivity was almost kept. This confirmed that the mixed oxides support played a crucial role in the enhancement for hydrogenation reaction.

Table 6. Effect of reaction temperature on the catalytic performance of the supported gold nanocatalysts in the selective hydrogenation of cinnamaldehyde.

Catalyst	T (°C)	Conversion (%)	Selectivity (%)			COL Yield (%)
			COL	HCOL	HCOL	
Au/ZnO	80	0.0	-	-	-	0.0
Au/ZnO	100	1.6	96.9	3.1	0.0	1.6
Au/ZnO	120	2.3	92.3	7.7	0.0	2.1
Au/ZnO	140	30.2	90.7	7.0	2.3	27.4
Au/Fe ₂ O ₃	80	1.6	84.0	16.0	0.0	1.3
Au/Fe ₂ O ₃	100	6.3	78.9	21.1	0.0	5.0
Au/Fe ₂ O ₃	120	16.7	71.7	28.3	0.0	12.0
Au/Fe ₂ O ₃	140	57.0	80.2	12.3	7.5	45.7
Au/Zn _{0.7} Fe _{0.3} O _x	80	2.2	96.5	3.5	0.0	2.1
Au/Zn _{0.7} Fe _{0.3} O _x	100	12.3	91.3	8.7	0.0	11.2
Au/Zn _{0.7} Fe _{0.3} O _x	120	29.8	90.3	8.2	1.5	26.9
Au/Zn _{0.7} Fe _{0.3} O _x	140	75.4	88.5	4.0	7.5	66.7
Au/Zn _{0.5} Fe _{0.5} O _x	80	0.0	-	-	-	0.0
Au/Zn _{0.5} Fe _{0.5} O _x	100	1.2	98.5	1.5	0.0	1.2
Au/Zn _{0.5} Fe _{0.5} O _x	120	2.1	96.3	3.7	0.0	2.0
Au/Zn _{0.5} Fe _{0.5} O _x	140	18.1	93.2	5.9	0.9	16.9

Reaction condition: catalyst (60 mg, Au: 0.32 mol %), CAL (1.6 mmol), nonane (0.8 mmol), isopropyl alcohol (15 mL), temperature (140 °C), H₂ (1.0 MPa), reaction time (10 h). The conversion and selectivity were determined by GC analysis with nonane as an internal standard.

Table 7. Comparison of catalytic results for cinnamaldehyde hydrogenation over gold nanocatalysts in the literature and in this work.

Catalyst	Solvent	Reaction Conditions	CAL Con. (%)	COL Sel. (%)	Reference
Au/ZnO-CP	Isopropanol	110 °C, 2.0 MPa, 40 min	94.9	100	[13]
Au/ZnO-DP	Isopropanol	140 °C, 1.0 MPa, 10 h	30.2	90.7	This work
Au-Ir/TiO ₂	Isopropanol	100 °C, 1.0 MPa, 1 h	12.0	83.4	[21]
Au/CeO ₂	Ethanol	120 °C, 1.0 MPa, 5 h	63.0	4.0	[3]
Cu-Au/SiO ₂	Ethyl acetate	100 °C, 2.0 MPa, 3 h	55.0	53.0	[42]
Au/Zn _{0.7} Fe _{0.3} O _x	Isopropanol	140 °C, 1.0 MPa, 10 h	75.4	88.5	This work

The reaction stability of Au/Zn_{0.7}Fe_{0.3}O_x catalyst was further investigated (Table 8). Using fresh Au/Zn_{0.7}Fe_{0.3}O_x catalyst, 74.6% conversion and 88.8% selectivity of COL was obtained in the first run. The results were very close to those in Table 4, indicating that Au/Zn_{0.7}Fe_{0.3}O_x nanocatalyst could be duplicated very well. In the second run, the use of recovered catalyst produced a very slightly decrease conversion (72.5%) but excellent selectivity of 87.3%. The catalyst was recovered again and used in the third run and fourth run, COL selectivity was kept intact and only CAL decreased slightly. This indicated that the Au/Zn_{0.7}Fe_{0.3}O_x nanocatalyst in this work showed good stability and could be used repeatedly.

Table 8. Reusability of the Au/Zn_{0.7}Fe_{0.3}O_x catalyst for CAL hydrogenation.

Run	Conversion (%)	Selectivity (%)		
		COL	HCOL	HCOL
1st	74.6	88.8	5.1	6.1
2nd	72.5	87.3	5.5	7.2
3rd	70.6	88.1	4.8	7.1
4th	67.8	87.9	5.3	6.8

Reaction condition: catalyst (60 mg, Au: 0.32 mol %), CAL (1.6 mmol), nonane (0.8 mmol), isopropyl alcohol (15 mL), temperature (140 °C), H₂ (1.0 MPa), reaction time (10 h). The conversion and selectivity were determined by GC analysis with nonane as an internal standard.

It has been reported that Au/ZnO displayed high selectivity to unsaturated alcohol in the selective hydrogenation of crotonaldehyde [17] and cinnamaldehyde [22] but low conversion at relatively low reaction temperature. In order to improve the conversion of Au/ZnO, we prepared ZnO-Fe₂O₃ mixed oxides supported gold nanocatalysts to catalyze the selective hydrogenation of cinnamaldehyde. It was found that Au/mixed oxides have larger surface area and better low temperature reduction ability than Au/ZnO. Among various ZnO-Fe₂O₃ mixed oxide supported gold nanocatalysts, Au/Zn_{0.7}Fe_{0.3}O_x exhibited the highest conversion of cinnamaldehyde and high selectivity to cinnamal alcohol. From the HAADF-STEM observation, it can be seen that the diameter distribution of gold particles on Au/Zn_{0.7}Fe_{0.3}O_x was the narrowest (0.5–4.5 nm) and the mean diameter (2.0 nm) was the smallest. The higher selective hydrogenation activity of Au/Zn_{0.7}Fe_{0.3}O_x than those of its counterparts suggests that smaller Au particles favor higher hydrogenation catalytic activity. This observation is in line with the well-known phenomenon that the catalytic property is tightly related to the size of Au particles and type of support materials [43–46]. It is widely accepted that the hydrogenation activity of gold nanocatalysts is mainly determined by the step of H₂ dissociation. The necessary condition for H₂ dissociation is the existence of low-coordinate Au atoms. Corma et al. presented evidence that H₂ adsorbs and dissociates with small activation barriers on low-coordinate Au atoms located at the corner positions on Au NPs [47,48]. Kaneda et al. found that in the deoxygenation of epoxides to alkenes over Au/HT nanocatalysts, the catalytic activities were remarkably increased with the decrease of average size of Au NPs on Au/HT nanocatalysts [49]. Small Au particles tend to contain a larger proportion of low-coordinated sites (steps, edges, and corners), providing more active sites for H₂ dissociation.

3. Materials and Methods

3.1. Material

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (A.R.), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (A.R.), Na_2CO_3 (A.R.), and NaOH (A.R.) were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (98%) was purchased from Accela. Cinnamaldehyde (98%) was purchased from Alfa Aesar (Haverhill, MA, USA). Isopropyl alcohol (99%) and nonane (99%) were purchased from Acros (Geel, Belgium). Nanopure water (resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$) was supplied by a Barnstead NANOpure Diwater™ system (Waltham, MA, USA). All chemicals were used without further purification.

3.2. Catalyst Preparation

$\text{ZnO-Fe}_2\text{O}_3$ mixed oxides were prepared by co-precipitation method. A mixed aqueous solution of $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ was heated at 70°C and then poured into an aqueous solution of Na_2CO_3 (1.2 times of the stoichiometric amount) which was pre-heated to 70°C . Then the suspension was stirred at 70°C for 1 h. The solid precursor was filtrated and washed with large amount distilled water to remove sodium ions. The prepared solid was dried at 120°C overnight and finally calcined in air at 300°C for 4 h. For comparison, single-component metal oxide ZnO and Fe_2O_3 were prepared by precipitation method.

Metal oxides supported gold nanocatalysts were prepared by deposition-precipitation (DP) method. An aqueous solution of HAuCl_4 was heated to 70°C and then the pH of solution was adjusted to 7 by adding aqueous NaOH solution. A desired amount of support with nominal gold loading of 2 wt % was added to the solution and then the pH was readjusted to 7 by adding aqueous NaOH solution. The suspension was further stirred at 70°C for 1 h. The solid precursor was filtrated, washed, and dried at 120°C overnight. Finally, the samples were calcined in air at 300°C for 4 h.

3.3. Catalyst Characterization

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical diffractometer (Empyrean, 4 kW) (Almelo, Netherlands), using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1543 \text{ nm}$) operated at 40 kV and 40 mA. 2θ scans were performed from 5° to 90° . The specific surface areas of the samples were measured by N_2 adsorption-desorption at 77 K on a Micromeritics ASAP 2020 analyzer (Atlanta, GA, USA) with the samples degassed at 250°C for 6 h under vacuum before measurement. The actual loading of gold was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) technique on the PerkinElmer ICP-OES 7300DV spectrometer (Waltham, MA, USA). High angle annular dark field (HAADF) images were acquired by using FEI Tecnai G2 F20 microscopy operated at 200 kV (Hillsboro, OR, USA). Hydrogen temperature programmed reduction (H_2 -TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics) (Atlanta, GA, USA). Before H_2 -TPR measurement, 0.05 g of catalyst was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 6 mm) and pretreated in an Ar flow of 50 mL/min at 300°C for 2 h. After being cooled at the same atmosphere to 40°C , the pretreated sample was exposed to a flow (50 mL/min) of 5% H_2/Ar for 1 h and then heated from RT to 800°C at a ramp of $10^\circ\text{C}/\text{min}$. The alteration in H_2 concentration of the effluent was monitored on-line by the chemical adsorption analyzer. X-ray photoelectron spectroscopy (XPS) were recorded at room temperature on a Thermo ESCALAB 250Xi spectrometer (Waltham, MA, USA) using Al K α ($h\nu = 1486.6 \text{ eV}$) as the excitation source.

3.4. Activity Measurement

The liquid-phase hydrogenation of cinnamaldehyde was carried out in a Teflon-lined stainless steel autoclave (25 mL). Typically, the autoclave was first introduced with reaction mixture containing 0.21 g cinnamaldehyde, 0.11 g n-nonane (internal standard), 15 mL isopropyl alcohol (solvent), 60 mg catalyst, and then purged with H_2 eight times. The catalytic reaction was carried out under

1.0 MPa H₂ and at 140 °C for 10 h. After reaction, the mixture was cooled down to room temperature and the catalyst was separated from the solution by filtration. The products in the solution were analyzed by a gas chromatograph (Agilent GC 7890B) equipped with a DB-1 capillary column (50 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

4. Conclusions

By using coprecipitation and deposition–precipitation methods, ZnO-Fe₂O₃ mixed oxides and ZnO-Fe₂O₃ mixed oxide supported gold nanocatalysts were prepared, respectively. Among all the gold nanocatalysts in this work, Au/Zn_{0.7}Fe_{0.3}O_x showed the highest conversion of cinnamaldehyde (75.4%) and high selectivity to cinnamal alcohol (88.5%). N₂ adsorption–desorption and HAADF-STEM characterizations showed that Au/Zn_{0.7}Fe_{0.3}O_x possessed high surface area of 136 m²/g, and large amount of highly dispersed small gold particles. On Au/Zn_{0.7}Fe_{0.3}O_x, 50% of gold particles are smaller than 2 nm, finally giving a small mean size of 2 nm. These characteristics endowed Au/Zn_{0.7}Fe_{0.3}O_x with a larger amount of exposed active gold atoms and good H₂ dissociation ability, which were responsible for the excellent catalytic performance of Au/Zn_{0.7}Fe_{0.3}O_x.

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