

# Selective Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol over Au Catalysts: Influence of the Oxide-Supports

Yifei Zhang<sup>1</sup> · Shaohua Zhang<sup>1</sup> · Xiaoli Pan<sup>1</sup> · Ming Bao<sup>2</sup> · Jiahui Huang<sup>1</sup> · Wenjie Shen<sup>1</sup>

Received: 23 August 2016 / Accepted: 27 October 2016 © Springer Science+Business Media New York 2016

Abstract Uniform Au particles with a mean size of 1.9 nm were initially synthesized with polyvinyl alcohol (PVA) as protecting agent, and then deposited on MgO,  $Al_2O_3$ ,  $TiO_2$ ,  $Fe_2O_3$ ,  $Co_3O_4$ , ZnO and  $In_2O_3$ . After calcinations at 300 °C in air to remove PVA, Au particles were highly dispersed and immobilized on all the supports, displaying narrow diameter distributions and almost identical mean sizes of 2.5–3.2 nm. The Au-oxides catalysts were further used to catalyze selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL). It was found that the selectivity of COL was tightly related to the acidity/

basicity of the Au/oxides catalysts. The catalyst with only acidic sites such as the Au/Al<sub>2</sub>O<sub>3</sub> catalyst gave very low selectivity of COL of 15%. The catalysts with only basic sites such as Au/MgO catalyst displayed medium selectivity of COL of 52%. Interesting, the Au catalysts with both acidic and basic sites such as the Au/In<sub>2</sub>O<sub>3</sub> and Au/ZnO catalyts exhibited the highest selectivity of COL of around 86%. The synergistic cooperation of acidic sites and basic sites should be responsible for preferential adsorption and activation of the C=O group than C=C group in CAL, and then preferential hydrogenation of C=O to COL.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10562-016-1901-8) contains supplementary material, which is available to authorized users.

Ming Bao mingbao@dlut.edu.cn

⊠ Jiahui Huang jiahuihuang@dicp.ac.cn

- <sup>1</sup> Gold Catalysis Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
- <sup>2</sup> State Key Laboratory of Fine Chemicals, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, China

#### **Graphical Abstract**



**Keywords** Gold catalysis · Selective hydrogenation · Cinnamaldehyde · Cinnamyl alcohol · Acidity/basicity

# **1** Introduction

Selective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes to  $\alpha$ ,  $\beta$ -unsaturated alcohols over heterogeneous catalysts has attracted increasing attentions in recent years, because of the wide application of the desired products in the synthesis of value-added fine chemicals. Fundamentally, this selective hydrogenation reaction has been viewed as one of the most challenging reactions in heterogeneous catalysis, primarily because of the difficult in selectivity control.  $\alpha$ ,  $\beta$ -unsaturated aldehydes contain both C=C and C=O groups, while the hydrogenation of C=C group occurs preferentially than that of the C=O group, and moreover the successive hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated alcohols to the fully saturated alcohols may also take place rapidly. Supported Pd and Pt catalysts have been typically used to catalyze selective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes. However, saturated aldehydes and even alcohols were produced as major product, rather than desired  $\alpha$ , β-unsaturated alcohols [1]. Gold catalysts have been demonstrated to selectively hydrogenate the C=O group in  $\alpha$ ,  $\beta$ -unsaturated aldehydes [2–12]. For example, Au/ZnO catalysts were reported to be effective for crotonaldehyde hydrogenation to crotonyl alcohol with a selectivity of 80% [3, 4] and acrolein hydrogenation to allyl alcohol with a selectivity of 63% [7, 8]. Au/CeO<sub>2</sub> effectively catalyzed the hydrogenation of different  $\alpha$ ,  $\beta$ -unsaturated aldehydes such as crotonaldehyde and cinnamaldehyde to corresponding  $\alpha$ ,  $\beta$ -unsaturated alcohols with selectivities of more than 80% [9]. In this respect, the selectivity of unsaturated alcohols is intimately linked to the size of Au particles and the nature of the oxide-support [5, 7, 11, 12].

The effect of Au particle size on the selectivity of unsaturated alcohols has been extensively examined, but controversial observations are frequently reported [5, 7, 11]. For instance, the selectivity of acrolein hydrogenation to allyl alcohol over Au/TiO2 and Au/ZrO2 catalysts increased with enlarging the size of Au particles in the range of 1.1-5.3 nm [7, 11], however, the selectivity of crotonaldehyde hydrogenation to crotyl alcohol over the Au/TiO<sub>2</sub> catalyst was independent of the size of Au particles in the range of 1.7-8.7 nm, being 60-70% [5]. One possible reason might be due to the wide size distribution of Au particles upon dispersing on the oxide supports through conventional preparation techniques such as deposition-precipitation, co-precipitation and impregnation, from isolated Au atoms, Au clusters (<2 nm), small particles (2–5 nm) to even large particles (>5 nm) [13, 14]. On the other hand, the investigation on the effect of the oxide-support on the selectivity of unsaturated alcohols over Au catalysts has been less examined. As the catalytic performance of Au catalysts is very sensitive to the size of Au particles, the wide size distribution of Au particles would heavily shadow the effect of the oxide-support on the selectivity of unsaturated alcohols.

The colloid-immobilization is a good method to prepare the supported Au catalysts with narrow Au size distribution because Au colloids with certain sizes are pre-synthesized by virtue of the protection of suitable

reagents such as thiols, poly(N-vinyl-2-pyrrolidone) (PVP) and polyvinyl alcohol (PVA). Compared with thiols and PVP, PVA is a better choice for Au NPs synthesis because it can be decomposed at the relative low temperature of 300 °C [15, 16]. Schüth et al. have utilized the colloid-immoblization method to deposit 3.0 nm Au colloids protected by PVA on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO and ZrO<sub>2</sub> [15] and 2.1 nm Au colloids protected by PVA on  $FeO_x$  [16], and the resulting Au catalysts displayed the narrow size distribution of Au particles. In this work, we used the colloid-immobilization strategy to study the effect of oxide-support on the catalytic performance of Au particles with uniform sizes in the selective hydrogenation of CAL to COL. Gold particles with a rather narrow diameter distribution were initially synthesized with PVA as the protecting reagent, and then dispersed on a series of oxides (MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>,  $Fe_2O_3$ ,  $Co_3O_4$ , ZnO, and  $In_2O_3$ ) with uniform sizes of 2.5-3.2 nm. A remarkable effect of the oxide-support on the selectivity of CAL hydrogenation to COL was observed. The ZnO- and In<sub>2</sub>O<sub>3</sub>-supported Au particles offered the prominent selectivity of COL of 82-87%, which is almost irrespective to the reaction temperature and period.

### 2 Experimental

### 2.1 Catalyst Preparation

Chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O), polyvinyl alcohol ( $M_w = 16,000$ ) and sodium borohydride (NaBH<sub>4</sub>) were purchased from Acros Chemical Company. Metal oxides MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (P25), Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, ZnO, and In<sub>2</sub>O<sub>3</sub> were purchased from Aladdin Chemical Company. Before the use, metal oxides were calcined at 300 °C in air.

Gold colloids were initially synthesized according to a typical procedure using PVA as protecting agent, and then the oxide-supported Au catalysts were prepared by a colloid-immobilization method [15, 16]. 20 mg HAuCl<sub>4</sub> was dissolved in 200 mL distilled water, and 4 mL 0.3 wt% PVA aqueous solution was added (PVA /Au=1.2/1.0 in weight ratio). After stirring at room temperature for 1.0 h, 5 mL 0.1 moL/L NaBH<sub>4</sub> aqueous solution was promptly added to the mixture, and Au<sup>3+</sup> species were immediately reduced into metallic Au species, and Au colloids were formed. After further stirring at room temperature for 1.0 h, 1.0 g oxide-support was added to Au colloids solution with an Au/support weight ratio of 1/100. The suspension



**Fig. 1** TEM image of Au colloids (**a**) and HAADF-STEM images of Au/MgO (**b**), Au/Al<sub>2</sub>O<sub>3</sub> (**c**), Au/TiO<sub>2</sub> (**d**), Au/Fe<sub>2</sub>O<sub>3</sub> (**e**), Au/Co<sub>3</sub>O<sub>4</sub> (**f**), Au/ZnO (**g**) and Au/In<sub>2</sub>O<sub>3</sub> (**h**). The *scale bar* corresponds to 20 nm

**Table 1** Physical properties ofthe Au catalysts

Au catalysts	Au/MgO	Au/Al <sub>2</sub> O <sub>3</sub>	Au/TiO <sub>2</sub>	Au/Fe <sub>2</sub> O <sub>3</sub>	Au/Co <sub>3</sub> O <sub>4</sub>	Au/ZnO	Au/In <sub>2</sub> O <sub>3</sub>
Au loading/wt.%	0.77	0.82	0.50	0.71	0.81	0.89	0.83
Au sizes/nm	$3.2 \pm 0.7$	$2.5 \pm 0.5$	$2.9\pm0.5$	$2.6 \pm 0.5$	$3.0 \pm 0.6$	$2.5\pm0.5$	$2.7\pm0.5$
BET surface area $/m^2/g^{-1}$	245.3	110.3	57.6	58.5	44.5	23.8	34.8

# Table 2Cinnamaldehydehydrogenation over the Aucatalysts

Catalyst	Temperature (°C)	CAL conv. (%)	Selectivi	ty (%)	COL yield (%)	
			COL	HCAL	HCOL	
Au/MgO	120	37	52	42	6	19
Au/Al <sub>2</sub> O <sub>3</sub>	120	99	15	2	79	15
Au/TiO <sub>2</sub>	120	99	8	15	70	8
Au/Fe <sub>2</sub> O <sub>3</sub>	120	62	65	27	8	40
Au/Co <sub>3</sub> O <sub>4</sub>	120	95	47	23	29	45
Au/ZnO	120	0	0	0	0	0
	150	23	86	11	3	20
	180	88	83	4	12	73
Au/In <sub>2</sub> O <sub>3</sub>	120	42	86	10	4	36
	150	70	86	8	5	60
	180	91	84	2	13	76

*Reaction conditions* 0.2 g Au catalyst and 1.6 mmoL CAL that was dissolved in 20 mL dioxane were added into the autoclave, and then the reaction was performed under 1.0 MPa  $H_2$  pressure at the required temperature for 18 h

COL cinnamyl alcohol, HCAL hydrocinnamaldehyde, HCOL hydrocinnamyl alcohol

was further stirred overnight at room temperature so that Au colloids could be completely deposited on the oxidesupport. The solid was collected by filtration, washed with distilled water, dried under vacuum at room temperature overnight, and finally calcined at 300 °C in air for 1.0 h, yielding the Au/oxides catalysts.

# 2.2 Characterizations

Transmission electron microscopy (TEM) was carried out on a Hitachi 7700 microscope operated at 120 kV. Highangle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed with a JEOL JEM-2100F microscope operated at 200 kV. Gold loadings on the catalysts were analyzed by inductively coupled plasma atomic absorption spectrometry (ICP-AAS, Plasma-Spec-II). Infrared spectroscopy (IR) of Au catalysts were recorded on a Bruker VEXTEX 70. BET surface area was measured on ASAP 2020 instrument. Before the measurement, the samples were degassed at 90 °C for 1 h and 250°C for 6 h. Temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR), desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD), and ammonia (NH<sub>3</sub>-TPD) were conducted with the same equipment. The detailed operation procedures are available in the Supporting Information.

# 2.3 Catalytic Tests

The selective hydrogenation of CAL was conducted in a 50 mL stainless steel autoclave under stirring. Typically, 0.2 g Au catalyst and 1.6 mmoL CAL that was dissolved in 20 mL dioxane were added into the autoclave. A small amount of octane was used as inner standard. The autoclave was purged with hydrogen for five times, pressurized to 1.0 MPa at room temperature, and heated to 120 °C under stirring (600 rpm). After reaction for a certain period, the products were analyzed by gas chromatography (GC, Agilent 7890B) equipped with a flame ionization detector and DB-1 capillary column (50 m×0.32 mm×0.25  $\mu$ m). For the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts, the reaction was further tested at 150–180 °C in order to examine the influence of reaction temperature on COL selectivity.

# 2.4 Results and Discussion

Figure 1 shows TEM image of Au colloids and HAADF-STEM images of Au/oxides catalysts. Gold colloids had a mean diameter of  $1.9 \pm 0.4$  nm with a very narrow size distribution (Fig. S1). Upon dispersion on the oxide-supports and thermal treatment at 300 °C for removing the PVA ligands (Fig. S2), Au particles were tightly immobilized on the oxides. The mean diameters of Au particles over all the six catalysts were almost identical, 2.5–3.2 nm, being independent on the chemical nature of the oxide-support (Table 1). It should be noted that the mean diameter of supported Au particles was just slightly larger than that of as-prepared Au colloids, indicating a minor aggregation of Au colloids during the immobilization and calcination processes. ICP analyses confirmed that the loadings of Au were in the range of 0.71–0.89 wt.% (Table 1), whereas Au/ TiO<sub>2</sub> was the only exception, which gave much lower Au loading of 0.50 wt.%.

Table 2 compares the performance of Au catalysts for the hydrogenation of CAL. On the Au/Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> catalysts, the complete conversion of CAL was readily achieved, but the main product was hydrocinnamyl alcohol (HCOL) with a selectivity more than 70% and the selectivity towards COL was less than 20%. On the Au/MgO, Au/  $Fe_2O_3$  and Au/Co<sub>3</sub>O<sub>4</sub> catalysts, the selective hydrogenation of the C=O group in CAL became the major route, giving the medium selectivity of COL in the range of 47-65%. Interestingly, the selective hydrogenation of the C=O group in CAL dominated the hydrogenation reaction over the Au/ In<sub>2</sub>O<sub>3</sub> catalyst, providing the highest selectivity of COL of 86% with a CAL conversion of 42%. As further raising the temperature to 150 °C and then 180 °C, the conversion of CAL significantly increased to 71 and 91%, respectively, but the selectivity of COL was kept unchanged, being 84-86%. Interestingly, the Au/ZnO catalyst showed a similar pattern to Au/In<sub>2</sub>O<sub>3</sub>. The only difference was that the Au/ZnO catalyst required a relatively higher temperature to initiate the reaction, but high selectivity of COL of about 86% was also achieved.

In order to elucidate unique properties of the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts with extraordinary selectivity towards COL, the reaction profiles over these two catalysts were examined, as shown in Fig. 2. The conversion of CAL was 17% at 3 h and gradually approached 88% at 18 h over the Au/ZnO catalyst, while the selectivity of COL was kept almost unchanged, which was in the range of 82–87% (Fig. 2a). The conversion of CAL over Au/In<sub>2</sub>O<sub>3</sub> increased more rapidly than that over Au/ZnO with time on stream. The conversion of CAL over Au/In<sub>2</sub>O<sub>3</sub> attained 43% at 3 h and 70% (the highest conversion of CAL) at 8 h, while the selectivity of COL was also kept stable, irrespective of the reaction time, which was in the range of 82–86% (Fig. 2b).

So far, supported Au catalysts have been popularly used to catalyze selective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes [2–12]. It is generally believed that the selectivity of unsaturated alcohols is closely linked to the size of Au particles and the nature of the oxide-supports [5, 7, 11, 12]. HAADF-STEM observations on the Au catalysts investigated here clearly identified that Au particles had almost identical mean diameters of 2.5–3.2 nm with very narrow size distributions (Fig. S1). Therefore, the influence of the size of Au particles on the selectivity of COL could be simply ruled out, while the significant variations in COL selectivity might be assigned to the difference in chemical nature of the oxide-supports.

Since the reducibility of the oxide-support was reported to remarkably alter the selectivity of unsaturated alcohols on Au catalyst [12], the redox properties of the Au/  $Fe_2O_3$  and Au/Co<sub>3</sub>O<sub>4</sub> catalysts were investigated by H<sub>2</sub>-TPR (Fig. 3). The Au/Fe<sub>2</sub>O<sub>3</sub> catalyst showed two broad



Fig. 2 Hydrogenation of CAL on the Au/ZnO (a) and Au/In<sub>2</sub>O<sub>3</sub> (b) catalysts. 0.2 g Au catalyst and 1.6 mmoL CAL that was dissolved in 20 mL dioxane were added into the autoclave, and then the reaction was performed under 1.0 MPa H<sub>2</sub> pressure at 180 °C for Au/ZnO and 150 °C for Au/In<sub>2</sub>O<sub>3</sub> for different period. *COL* cinnamyl alcohol, *HCAL* hydrocinnamaldehyde, *HCOL* hydrocinnamyl alcohol



Fig. 3 H2-TPR profiles of the Au/Fe2O3 and Au/Co3O4 catalysts

reduction peaks, and one low-temperature reduction peak centered at 385 °C was assigned to the reduction of Fe<sup>3+</sup> species to Fe<sup>2+</sup> species, while the broad reduction peak at above 400 °C was ascribed to the subsequent reduction of FeO to metallic Fe [12]. The Au/Co<sub>3</sub>O<sub>4</sub> catalyst displayed one shoulder peak at about 330 °C and one strong peak centered at 440 °C. The former peak was ascribed to Co<sub>3</sub>O<sub>4</sub> reduction to CoO and the latter peak was assigned to CoO reduction to metallic Co [17]. As shown in Table 2, the Au/ Fe<sub>2</sub>O<sub>3</sub> and Au/Co<sub>3</sub>O<sub>4</sub> catalysts with typical reducible features only displayed medium selectivities of 47 and 65% for COL, which are still much lower than those obtained on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts. Therefore, the reducibility of the oxide-supports might not be the main factor to determine the selectivity of COL in this work.

It has been reported that the introduction of Lewis acid such as Fe and Sn cations to the  $Pt/SiO_2$  catalyst markedly enhanced the selectivity of allyl alcohol in acrolein hydrogenation [1]. Similarly, the introduction of Lewis acid Mo, W, Nb, Fe and Re cations to  $Ir/SiO_2$  catalysts was also confirmed to promote the selectivity of crotyl alcohol during crotonaldehyde hydrogenation [18, 19]. It was presumed that metal cations on the oxide-support adsorbed and activated the C=O group in the substrates while noble metal particles dissociatively activated hydrogen molecules and the resulting atomic hydrogen species reacted with the activated C=O group to form unsaturated alcohol. Accordingly, the acidity and basicity of the Au/oxide catalysts in this work was analyzed by NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD.



**Fig. 4**  $NH_3$ -TPD (**a**) and CO<sub>2</sub>-TPD (**b**) profiles of the Au catalysts. The signals of  $NH_3$ -TPD and CO<sub>2</sub>-TPD were recorded by TCD detector and mass spectroscopy, respectively

In Fig. 4a, the Au/MgO catalyst did not give desorption peak of NH<sub>3</sub>, indicating the absence of acidic sites, while it displayed two strong desorption peaks of CO<sub>2</sub> in the temperature range of 50–200 and 200–400 °C in Fig. 4b. The former peak was caused by the decomposition of bicarbonates species formed by the reaction of CO<sub>2</sub> and surface hydroxyl groups, and the latter peak indicated the presence of the medium basicity caused by oxygen in Mg<sup>2+</sup> and O<sup>2-</sup> pairs [20, 21]. In Fig. 4a, the Au/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited two broad desorption peaks of NH<sub>3</sub> in the temperature range of 80–175 and 175–420 °C, respectively, similar to those present on Pt/Al<sub>2</sub>O<sub>3</sub> during NH<sub>3</sub>-TPD



Scheme 1 A possible pathway of CAL hydrogenation on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts. CAL cinnamaldehyde

analysis, indicating the presence of acidic sites with different strength [22]. In Fig. 4b, the Au/Al<sub>2</sub>O<sub>3</sub> catalyst showed an intense desorption peak of CO<sub>2</sub> in the temperature range of 50–200 °C centered at around 90 °C. This was caused by the decomposition of large amount of bicarbonates species and thus indicates the presence of a large quantity of surface hydroxyl groups on the Au/Al<sub>2</sub>O<sub>3</sub> catalyst [23]. Usually  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contains a large amount of Lewis acid sites [24], and in this work Al<sub>2</sub>O<sub>3</sub> with gamma phase was used as the support. Thus, it might be deduced that the Au/Al<sub>2</sub>O<sub>3</sub> catalyst processes both weak Bronsted acid sites (surface hydroxyl groups) and strong Lewis acid sites.

In Fig. 4a, the Au/ZnO catalyst gave a broad but relative weak desorption peak of NH<sub>3</sub> in the temperature range of 300-490 °C, indicating the presence of small amount of strong acidic sites, probably strong Lewis acid sites caused by Zn<sup>2+</sup> cations [25]. In Fig. 4b, the Au/ZnO catalyst displayed one very weak desorption peak of CO<sub>2</sub> at around 90 °C, meaning the presence of very small amount of surface hydroxyl groups, and one desorption peak of  $CO_2$  in the temperature range of 300-500 °C, probably ascribed to strong basic sites caused by low coordination oxygen anions [20, 21]. In Fig. 4b, the Au/In<sub>2</sub>O<sub>3</sub> catalyst exhibited one weak desorption of CO2 at around 90°C, caused by surface hydroxyl groups, and one desorption of CO<sub>2</sub> in the temperature range of 120-220 °C centered at 170 °C, indicating the presence of basic sites with medium strength, probably oxygen in  $In^{3+}$  and  $O^{2-}$  pairs [20, 21]. In Fig. 4a, the Au/In<sub>2</sub>O<sub>3</sub> catalyst displayed a broad desorption peak of NH<sub>3</sub> in the temperature range of 75–305 °C, indicating the presence of acidic sites with different strength, probably weak Bronsted acid sites (surface hydroxyl groups) and medium Lewis acid sites caused by  $In^{3+}$  cations [26].

Based on NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD measurements, it becomes clear that the Au/MgO catalyst had only basic sites with medium strength, while the Au/Al<sub>2</sub>O<sub>3</sub> catalyst possessed only acidic sites, including weak Bronsted acid sites and strong Lewis acid sites. However, the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts were characterized by both acidic and basic sites. The Au/ZnO catalysts possessed strong Lewis acid sites (Zn<sup>2+</sup> cations) and strong basic sites (low coordination oxygen anions). The In<sub>2</sub>O<sub>3</sub> catalysts had Lewis acid sites with medium strength (In<sup>3+</sup> cations) and the basic sites with medium strength (oxygen in In<sup>3+</sup> and O<sup>2-</sup> pairs), as well as a small amount of weak Bronsted acid sites (surface hydroxyl groups). Therefore, there may exist Lewis acidbase (M<sup>+</sup>–O<sup>-</sup>) pairs on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts.

Considering the fact that the Au/Al<sub>2</sub>O<sub>3</sub> catalyst gave only a very low selectivity of COL of 15%, much lower than that of the Au/MgO catalyst (Table 2), it might be deduced that the acidic sites on the Au catalysts could not guarantee the achievement of high selectivity of COL. In addition, the fact that the Au/MgO catalyst gave much lower selectivity of COL of 52% than that of the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts of above 80% might suggest that the basic sites on the Au catalysts could not yet guarantee the achievement of high selectivity of COL. Therefore, it seems that there is a close relation between high selectivity of unsaturated alcohols (Table 2) and the acidity/basicity of the Au catalysts (Fig. 4). As described above, two prerequisites should be fulfilled to achieve a higher selectivity towards COL: one is preferential hydrogenation of C=O to C=C and the other is the suppression of successive hydrogenation of COL to HCOL. As shown in Fig. 2, CAL conversion monotonously increased on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts with extending the reaction time, but the selectivity of COL was kept also consistent of above 80%. This indicates that the C=O group in CAL was preferentially adsorbed and activated over the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts. Furthermore, even after the formation of unsaturated alcohols (COL), successive hydrogenation of remaining C=C group in COL did not occur obviously.

This phenomenon demonstrates that the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts not only favored the preferential hydrogenation of C=O to C=C, but also effectively inhibited the successive hydrogenation of COL to HCOL. It is most likely that there exists a synergistic effect between the acidic and the basic sites on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts, which cooperatively favored the adsorption and activation of the C=O group, instead of the C=C group. Accordingly, the possible reaction pathway for the hydrogenation of CAL on the Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts is illustrated in Scheme 1. The C=O group in CAL was preferentially adsorbed and activated by Lewis acid-base  $(M^+-O^-)$  pairs at the perimeter interface between Au particle and the supports (ZnO and In<sub>2</sub>O<sub>3</sub>). Meanwhile, molecular hydrogen was dissociated on the surface of Au particles and the resulting atomic hydrogen species reacted with the activated C=O group, forming COL.

### **3** Conclusions

Gold particles with sizes of 2.5–3.2 nm were uniformly dispersed on a series of oxides through a colloid-immobilization strategy. The resulting Au catalysts were tested for the hydrogenation of CAL, and it was found that the acidic-basic properties of the oxide-support affected the selectivity of COL significantly. The Au/ZnO and Au/In<sub>2</sub>O<sub>3</sub> catalysts provided the highest selectivity of COL of about 86%, primarily because of the proper acidity and basicity. By virtue of the synergistic cooperation between the acidic and basic sites, the C=O group in CAL was preferentially activated and hydrogenated, while the successive hydrogenation of COL to HCOL was effectively suppressed.

Acknowledgements This work was financially supported by the Young Thousand Talents Program of China, the "Strategic Priority Research Program" of the Chinese Academy of Sciences (XDA09030103), and National Natural Science Foundation of China (No. 21473186).

# References

- 1. Ponec V (1997) Appl Catal A 149:27-48
- 2. Okumura M, Akita T, Haruta M (2002) Catal Today 74:265-269
- 3. Bailie JE, Hutchings GJ (1999) Chem Commun 21:2151-2152
- Bailie JE, Abdullah HA, Anderson JA, Rochester CH, Richardson NV, Hodge N, Zhang J, Burrows A, Kiely CJ, Hutchings GJ (2001) Phys Chem Chem Phys 3:4113–4121
- 5. Zanella R, Louis C, Giorgio S, Touroude R (2004) J Catal 223:328–339
- 6. Campo B, Petit C, Volpe MA (2008) J Catal 254:71-78
- 7. Mohr C, Hofmeister H, Claus P (2003) J Catal 213:86-94
- Mohr C, Hofmeister H, Radnik J, Claus P (2003) J Am Chem Soc 125:1905–1911
- Wang MM, He L, Liu YM, Cao Y, He HY, Fan KN (2011) Green Chem. 13:602–607
- Zhu Y, Tian L, Jiang Z, Pei Y, Xie SH, Qiao MH, Fan KN (2011) J Catal 281:106–118
- 11. Claus P, Brückner A, Mohr C, Hofmeister H (2000) J Am Chem Soc 122:11430–11439
- Milone C, Ingoglia R, Schipilliti L, Crisafulli C, Ner G, Galvagno S (2005) J Catal 236:80–90
- Herzing AA, Kiely CJ, Carley AF, Landon P, Hutchings GJ (2008) Science 321:1331–1335
- Ta N, Liu JY, Chenna S, Crozier PA, Li Y, Chen AL, Shen WJ (2012) J Am Chem Soc 134:20585–20588
- 15. Comotti M, Li WC, Spliehoff B, Schüth F (2006) J Am Chem Soc 128:917–924
- Liu Y, Jia CJ, Yamasaki J, Terasaki O, Schüth F (2010) Angwe Chem Int Ed 49:5771–5775
- 17. Xue WJ, Wang YF, Li P, Liu ZT, Hao ZP, Ma CY (2011) Catal Commun 12:1265–1268
- Tamura M, Tokonami K, Nakagawa Y, Tomishige K (2016) ACS Catal 6:3600–3609
- Yu Q, Bando KK, Yuan JF, Luo CQ, Jia AP, Hu GS, Lu JQ, Luo MF (2016) J Phys Chem C 120:8663–8673
- 20. Chen J, Tian SH, Lu J, Xiong Y (2015) Appl Catal A 506:118–125
- 21. Hu JC, Zhu KK, Chen LF, Kubel C, Richards R (2007) J Phys Chem C 111:12038–12044
- 22. Paulis M, Peyrard H, Montes M (2001) J Catal 199:30-40
- Santos RCR, Pinheiro AN, Leite ER, Freire VN, Longhinotti E, Valentini A (2015) Mater Chem Phys 160:119–130
- Feng R, Liu ST, Bai P, Qiao K, Wang YH, Al-Megren HA, Rood MJ, Yan ZF (2014) J Phys Chem C 118:6226–6234
- Yu Q, Zhang XY, Li B, Lu JQ, Hu GS, Jia AP, Luo CQ, Hong QH, Song YP, Luo MF (2014) J Mol Catal A 392:89–96
- 26. Ajaikumar S, Pandurangan A (2009) Appl Catal A 357:184-192