



Article Efficient Synthesis of Methyl Methacrylate by One Step Oxidative Esterification over Zn-Al-Mixed Oxides Supported Gold Nanocatalysts

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Abstract: Methyl methacrylate (MMA) is an important monomer in fine chemicals. The synthesis of MMA by one-step oxidative esterification from methacrolein with methanol over a heterogeneous catalyst with high activity, selectivity and stability is highly desirable. Herein, Zn-Al-hydrotalcites (HTs)-supported atomically precise Au_{25} nanoclusters with different molar ratios of Zn^{2+}/Al^{3+} were prepared and used as the precursors for this reaction. They exhibited good performances in comparison with the gold catalysts prepared by the deposition precipitation method. The structural and electronic properties were evaluated by various characterization technologies, including X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) of CO adsorption, X-ray photoelectron spectroscopy (XPS), and CO₂ temperature-programmed desorption (TPD). The combined characterization results suggested that the adsorption property of gold and the basicity of the catalyst contributes to their high activities. Substrates extended experiments and stability tests implied the potential application of Zn-Al-mixed oxides supported gold catalysts, which paves a new way for supported gold catalyst in the one-step oxidation esterification reaction.

Keywords: gold cluster; hydrotalcite; methacrolein; methyl methacrylate; oxidative esterification

1. Introduction

Methyl methacrylate (MMA) is an important monomer for the synthesis of polymethyl methacrylate (PMMA), which is widely used for producing acrylic plastic [1]. A recent analysis originated from the global MMA market indicated that the demand for MMA may reach \$9.8 billion by 2027 [2]. Thus, a noteworthy growth in MMA monomers will appear in the next several years. Traditionally, the dominant industrial process for the synthesis of MMA has been the acetone cyanohydrin (ACH) route [3], in which acetone and hydrocyanic acid are used as the raw materials. At the same time, the ACH process involves environmentally unfriendly issues that employ strong sulfuric acid as a catalyst and inevitably generate ammonium bisulfate waste [3,4].

Currently, isobutene (IB) oxidation routes that stem from isobutene and C4 ingredients for producing MMA are attracting great interest due to the economic and environmental preponderance [5,6]. In these processes, isobutene is first oxidized to methacrolein (MAL) and then oxidized to methacrylic acid (MAA), followed by esterification of MAA to MMA [5]. Instead, MAL could also react with methanol to form MMA by one-step oxidative esterification (Scheme 1) [6]. In view of energy efficiency and environmental



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). cost, the direct oxidative esterification process is more attractive in comparison with the two-step method. However, it is still very challenging for the development of efficient and selective catalytic systems under moderate conditions by a one-step method [7,8].



Scheme 1. Isobutene oxidation routes to produce methyl methacrylate (MMA).

Supported gold catalysts are generally believed to exhibit good performances in oxidation reactions under moderate conditions [9-14]. The special property enables it to be a potential candidate to replace traditional Pd-based catalysts in one-step oxidative esterification [15-22]. Previously, K. Suzuki at Asahi Kasei developed a SiO₂-Al₂O₃-MgO multiple oxides-supported AuNiO_x catalyst with core–shell structure [15]. The catalyst showed good performance for MAL to MMA, with the conversion of $\sim 60\%$ and selectivity of 96–97%. After this, Wang et al. observed good activity and selectivity over the Au/MgO catalyst, which showed conversion of 98% and selectivity of 99%, respectively [16]. Moreover, gold catalysts supported on different transition metal oxides and hydroxyapatite have been prepared in this reaction to evaluate the catalytic performances [17–22]. Their comparing results are shown in Table S1. Based on these results, the property of the support and/or the particle size of gold has been demonstrated to be crucial for one-step oxidative esterification [16,17,21]. The support with strong basic sites and the gold with a small average particle size are said to benefit the transformation of MAL to MMA [16,21]. However, although the activity and selectivity of supported gold catalysts exhibited great advantages to traditional Pd-based catalysts, the stability was among one of the big challenges.

Recently, layered double hydroxides (HTs) or hydrotalcite-type compounds, which have a general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+} \cdot [(A^{n-})_{x/n}] \cdot yH_2O$, have attracted great interest due to their high surface area, homogeneously dispersed metal atoms and acid-base properties [23–25]. Up to now, they have been utilized in a wide variety of oxidative reactions, such as the oxidation of benzyl alcohol [26], the oxidative steam reforming of methanol [27], the styrene epoxidation [28] and, etc. Previously, Zn-Al-mixed oxide-supported gold catalysts were demonstrated by us to display special catalytic performances in selective hydrogenation reactions [29–31]. The interaction between the gold and the support made it a great candidate for the synthesis of gold catalysts with controllable sizes [29,31]. Moreover, the inert activation for the vinyl group enables it a potential nominee for selective hydrogenation or oxidation reaction.

Herein, to synthesize the gold catalyst with homogeneous size, atomically precisely Au₂₅ nanoclusters were preliminarily prepared to use as a precursor; Zn-Al hydrotalcites with different Zn^{2+}/Al^{3+} molar ratios were used as the precursors of supports. The catalysts were applied for one-step oxidative esterification of methacrolein with methanol to the synthesis of MMA. In comparison with the catalytic performances of gold catalysts prepared by the deposition precipitation method, the Au₂₅/Zn_xAl-400 (x = 3,2,1) catalysts exhibited comparable better activity. N₂-physical adsorption–desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) of CO adsorption, X-ray photoelectron spectroscopy (XPS) and CO₂ temperature-programmed desorption (TPD) were utilized to characterize

the structural and electronic properties of the catalysts, from which the relationship about the structure and catalytic performances were reasonably revealed.

2. Results and Discussion

2.1. Catalytic Performances

Zn-Al-HTs with different molar ratios supported gold nanoclusters were used as the precursors of the catalysts. Their catalytic performances were successively investigated in one-step oxidative esterification of MAL with methanol (MeOH) for the synthesis of MMA (Scheme 2).

$$\begin{array}{c} O \\ HC'' \\ C = CH_2 + CH_3OH \end{array} \xrightarrow{Au \text{ catalyst}} H_3COC' \\ H_3C' \\ MAL \end{array} \xrightarrow{H_3COC'} C = CH_2 + H_3C \\ MMA \\ MMA \\ ACE \end{array} \xrightarrow{H_3C} CH_2 + Others$$

Scheme 2. Reaction pathway of methacrolein (MAL) with MeOH to form MMA.

From the results, the supported gold catalyst with Zn^{2+}/Al^{3+} molar ratio of 3 showed conversion of 84.9% and selectivity of 95.1% as the reaction was conducted at 353 K and 3 atm O₂ for 2 h. (Table 1, entry 1). When the Zn^{2+}/Al^{3+} ratio decreased from 3 to 2, the conversion of MAL increased to 93.1%, with the selectivity of MMA maintained at 94.8% (Table 1, entry 2). Further decreased the Zn^{2+}/Al^{3+} ratio to 1, both the activity and selectivity reduced, with the value being 90% and 92%, respectively (Table 1, entry 3). To be noted, although the final conversion of MAL was the highest over the Au₂₅/Zn₂Al-400 catalyst, the turnover frequency (TOF) based on total gold metals was slightly lower than that of the Au₂₅/Zn₃Al-400 and Au₂₅/Zn₁Al-400 catalysts. The reason may be originated from the influence of the Zn²⁺/Al³⁺ molar ratio on the adsorption of reactant, which leads to the difference of initial reaction rate to final reaction rate.

Table 1. Catalytic activities of MAL with MeOH to form MMA over supported gold catalysts.

Enter	Catalysts	Conversion (%) ^a	Selectivity (%) ^a			TOF(1-1)h
Entry			MMA	ACE	Others	$10F(n^{-1})^{\circ}$
1	Au ₂₅ /Zn ₃ Al-400	84.9	95.1	0.7	4.2	1734
2	$Au_{25}/Zn_2Al-400$	93.1	94.8	0.8	4.4	1626
3	$Au_{25}/Zn_1Al-400$	90.1	92.0	0.5	7.5	1675
4	$Au/Zn_2Al-400$	57.1	94.1	3.4	2.5	684
5	Zn ₃ Al-400	6.4	0	99.0	-	-
6	Zn ₂ Al-400	13.2	0	94.8	-	-
7	$Zn_1Al-400$	16.9	0	91.0	-	-
8	Blank	0	-	-	-	-

Reaction conditions: MAL/MeOH = 1/23(molar ratio), V(MeOH) = 4.5 mL, Catalyst: 0.1 g (Au: 0.1 mol%), T = 353 K, P_{O2} = 3 atm, t = 2 h. ^a Conversion and selectivity were analyzed by gas chromatography; ^b turnover frequency (TOF) of different catalysts was measured by moles of converted MAL per mole of gold per hour, with the conversion of MAL below 20%.

Hence, to study the evolution of the product distribution during the reaction process of MAL with MeOH, the dynamic experiments were carried out on the Au₂₅/Zn_xAl-400 catalysts with various Zn²⁺/Al³⁺ molar ratios. The yields of MAL and products with reaction time were plotted in Figure 1a–c. From the results, the product distributions over the three catalysts were similar within the reaction progress. After prolonging the reaction time, MMA was formed as the sacrifice of MAL. In the meantime, few acetals and byproducts appeared via the reaction of MAL and impurity aldehyde with MeOH (Figure S1). The reaction rates over the three catalysts decreased gradually from beginning to end, suggesting the dependence of activity on the concentration of the reactant. However, the selectivity of MMA could be well maintained at above 90% despite the various Zn²⁺/Al³⁺ ratios.



Figure 1. The products distributions of reaction with time courses over the (**a**) $Au_{25}/Zn_3Al-400$; (**b**) $Au_{25}/Zn_2Al-400$ and (**c**) $Au_{25}/Zn_1Al-400$ catalysts. Reaction conditions: MAL/MeOH = 1/23 (molar ratio), catalyst: 0.05 g, temperature: 353 K, O₂ pressure: 3 atm.

Under the same conditions, the supported gold catalysts prepared by the traditional deposition–precipitation (DP) method were synthesized for this reaction to make a comparison. The results are shown in Table 1, entry 4, with Zn^{2+}/Al^{3+} molar ratios of 2. As seen, the conversion of MAL over the Au/Zn₂Al-400 catalyst was 57.1%, which fell much lower than that of the Au₂₅/Zn_xAl-400. Simultaneously, the TOF value was several times lower than that of the Au₂₅/Zn_xAl-400. It suggested that the utilization of Au₂₅ nanoclusters as the precursor of gold greatly improves the activity. Following characterizations about the geometric and electronic structure of the gold catalysts were provided to reveal the structure–activity relationship.

Moreover, to disclose the effect of support for this reaction, the heat-treated Zn_xAl -HTs at 400 °C were also applied in this reaction under the same conditions (Table 1, entry 5–7). As seen, although 6.4%, 13.2% and 16.9% of the MAL conversions were observed over the Zn_3Al -400, Zn_2Al -400 and Zn_1Al -400 samples, no target product of MMA appeared in the system. It indicated the significant role of gold species towards one-step oxidative esterification of MAL to MMA. Moreover, to eliminate the effect of device deviation, the blank experiment with no catalysts or supports was conducted at the same condition (Table 1, entry 8). Almost no transformation of MAL to MMA could be observed, indicating the reaction between MAL and MeOH indeed occurred on our catalysts. To be noted, when compared the catalytic performance of Au_{25}/Zn_2Al -400 with the other catalysts in previous work, the activity and selectivity of our catalysts were among one the best-performing catalysts under similar conditions. Such results are shown in Table S1.

2.2. Structure of the Catalysts

The chemical analysis of Zn-Al-mixed oxides supported gold catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The loadings of gold on the Au₂₅/Zn₃Al-400, Au₂₅/Zn₂Al-400, Au₂₅/Zn₁Al-400 and Au/Zn₂Al-400 catalysts after heat treatment were 1.3, 1.2, 1.3 and 1.3 wt%, respectively, which agreed well with the nominal values. The actual molar ratios of Zn²⁺/Al³⁺ were 3.3, 2.4 and 1.2, respectively, with the content of Zn²⁺ and Al³⁺ of 21–32 wt% and 3.3–7.4 wt%, respectively (Table S2). The pore structure parameters such as the specific surface area, the pore volume and pore width were evaluated by the N₂-physical adsorption–desorption test (Table 2). The isotherms were exhibited in Figure S2. Based on the classification of IUPAC [32,33], the above catalysts exhibited typical IV type isotherms with obviously H3-type hysteresis loop, suggesting that the mesoporous structures existed in the above catalysts, which may result from the collapse of hydrotalcites structure after heat treatment.

Entry	Catalyst	Loadings of Gold (wt %) ^a	Surface Area (m²/g) ^b	Pore Volume (cm ³ /g) ^c	Half Pore Width (nm) ^d	Particle Size of Gold (nm) ^e	Total Basicity (μmol CO ₂ /g _{cat}) ^f
1	Au ₂₅ /Zn ₃ Al-400	1.27	49.1	0.24	1.71	2.8	640
2	$Au_{25}/Zn_2Al-400$	1.18	60.5	0.14	1.53	2.5	500
3	$Au_{25}/Zn_1Al-400$	1.32	80.9	0.27	1.71	2.5	430
4	$Au/Zn_2Al-400$	1.32	71.0	0.08	1.90	2.8	540

Table 2. Textural properties of Zn-Al-mixed oxides supported gold nanoclusters.

^a The actual loadings of gold were evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement. ^b Surface area was calculated from the Brunauer-Emmet-Teller (BET) equation at P/P_0 range of 0.05–0.3. ^c Total pore volume was calculated at $P/P_0 = 0.98$. ^d Pore width was calculated from the adsorption branch of the isotherm—BJH. ^e The mean particle sizes of gold were calculated from TEM measurements. ^f Total basicity was calculated from CO₂–TPD.

> The crystallographic phases of the catalysts before and after calcination were analyzed by powder XRD. The patterns are shown in Figure 2. Before the thermal treatment, all of the catalysts exhibited the characteristic reflections of the hydrotalcite lamellar structure with intense diffraction peaks at 11.7°, 23.6°, 34.6°, 39.7°, 46.8°, 60.4° and 61.8° (Figure 2a). These peaks could be assigned to (003), (006), (012), (015), (018), (110) and (113) planes of standard zinc-aluminum hydrotalcite (JCPDS NO. 00-048-1023). After calcination, the lamellar structure of hydrotalcites went into collapse, with the formation of Zn-Almixed oxides. The XRD patterns of the samples after heat treatment at 400 °C are shown in Figure 2b, in which obvious sharp peaks corresponding to reflections of ZnO phase (JCPDS NO. 01-089-0510) were observed, with the peaks located at around 32.1°, 34.6°, 36.5°, 47.6°, 56.8° and 62.7°. It demonstrated that Zn and Al atoms were homogeneously distributed in the framework of the catalysts. Noteworthy, no diffraction peaks ascribed as face-centered cubic gold were observed in all of the catalysts, perhaps due to the small particle sizes or low concentration of Au.



Figure 2. XRD patterns of Zn-Al-HTs supported gold nanoclusters before (a) and after (b) heat treatment.

In order to examine the particle sizes and lattice parameters of gold, TEM and HRTEM were performed on the Au₂₅/Zn_xAl-400 (x = 3, 2, 1) and Au/Zn₂Al-400 (DP) catalysts (Figure 3). More than 200 nanoparticles in representative regions were included to count the average particle sizes. As shown from TEM images, all of the gold particles after thermal treatment were uniformly dispersed on the catalysts, with similar particle sizes of 2.8 ± 0.7 nm (Figure 3a₁), 2.5 ± 0.8 nm (Figure 3b₁), 2.5 ± 0.7 nm (Figure 3c₁) and 2.8 ± 0.9 nm (Figure 3d₁) over the Au₂₅/Zn₃Al-400, Au₂₅/Zn₂Al-400, Au₂₅/Zn₁Al-400 and Au/Zn₂Al-400 catalysts, respectively. Moreover, the gold particles with the shape of hexagon, sphere or ellipsoid could be observed, with clear boundaries between gold and



supports. The interplanar spacing of 2.42 Å, 2.60 Å and 2.80 Å corresponded to (101), (100) and (002) lattice fringes of the supports that were consistent with the XRD results.

 $\label{eq:Figure 3. TEM (a_1-d_1) and HRTEM (a_2-d_2) images of supported gold catalysts: (a_{1-2}) Au_{25}/Zn_3Al-400; (b_{1-2}) Au_{25}/Zn_2Al-400; (c_{1-2}) Au_{25}/Zn_1Al-400; (d_{1-2}) Au/Zn_2Al-400 (deposition-precipitation (DP)).$

2.3. Electronic Property of the Catalyst

The in situ DRIFTS of CO adsorption was conducted to characterize the state of gold and active species on the surface of the $Au_{25}/Zn_xAl-400$ and $Au/Zn_2Al-400$ catalysts (Figure 4). The double peaks at 2119 and 2168 cm⁻¹ could be ascribed to the adsorption of the gas phase CO, which disappeared gradually with the purging of helium. An obvious band at around 2102–2105 cm⁻¹ was presented in the $Au_{25}/Zn_xAl-400$ catalysts (Figure 4a–c). It could be ascribed to the CO molecule adsorbed on metallic gold [34]. Whereas on the $Au/Zn_2Al-400$ catalyst, no adsorption peak of CO was observed in the spectra except for the gaseous CO, indicating the adsorption of CO was very weak on the $Au/Zn_2Al-400$ catalyst (Figure 4d). That may result in the poor activity of $Au/Zn_2Al-400$ in oxidation esterification than that of the $Au_{25}/Zn_xAl-400$ (x = 3, 2, 1) catalysts.



Figure 4. In situ diffuse reflectance infrared Fourier–transform spectroscopy of CO adsorption (CO–DRIFT) spectra of supported gold catalysts: (a) $Au_{25}/Zn_3Al-400$; (b) $Au_{25}/Zn_2Al-400$; (c) $Au_{25}/Zn_1Al-400$; (d) $Au/Zn_2Al-400$ (DP).

The valence state of gold was also provided by X-ray photoelectron spectra (XPS). Figure 5 displayed a wide spectrum of the core levels of Au, Zn, Al, C, O (Figure 5a) and the high-resolution XPS spectra of Au 4f, C 1s, Zn 2p, Al 2p and O 1s on the Au₂₅/Zn_xAl-400 catalysts. Although part of the peak of Au 4f_{5/2} was overlapped by the signal of Zn 3p (Figure 5b), the branches of Au $4f_{7/2}$ could be deconvoluted from the peak. Obviously, the metallic gold (Au⁰) dominates the surface of gold species, with the binding energy at around 83.5 eV, which agreed well with the in situ CO DRIFT spectra. Moreover, three deconvoluted peaks located at about 288.3, 285.6 and 284.0 eV were presented in C 1s XPS spectra (Figure 5c), which could be assigned to the C=O, C–O and C–C bonds [35]. It indicated there were still carbonate on the catalysts even after high-temperature calcination at 400 °C. Additionally, O 1s XPS fitting results displayed the existence of O^{2-} , O–H and C=O species [36,37], which are named O_{α} , O_{β} and O_{γ} , respectively (Figure 5f). The lattice oxygen of O_{α} bounded to the metal cation of Zn^{2+} and Al^{3+} , which was supported by Zn 2p (Figure 5d) and Al 2p (Figure 5e) XPS spectra. To be noted, with decreasing of Zn^{2+}/Al^{3+} molar ratios, the valence state of Zn, Al, O species varied correspondingly, indicating the slight variation of the structure over the Zn-Al mixed oxides. Moreover, the oxygen in the form of a hydroxyl group (O_{β}) provided some basic sites of the catalysts that may promote the reaction since the abundance of previous works highlights the effect of basicity for catalytical performances [16,19,38].



Figure 5. (a) XPS wide spectra and (b) Au 4f, (c) C 1s, (d) Zn 2p, (e) Al 2p (f) O 1s of XPS spectra over the Au₂₅/Zn_xAl-400 catalyst: (1) Zn²⁺/Al³⁺ = 1; (2) Zn²⁺/Al³⁺ = 2; (3) Zn²⁺/Al³⁺ = 3.

2.4. The Basic Property of the Catalyst

Previously, several groups have presented the significance of basicity towards oxidative esterification of MAL with methanol [16,19,38]. It was said that the catalysts with a large density of basic sites could accelerate the formation of hemiacetal intermediate, thus, contribute to the formation of MMA [16,38]. To analyze the basicity of the supported gold catalyst, CO₂ temperature-programmed desorption (TPD) was subsequently employed on the Au₂₅/Zn_xAl-400 and Au/Zn₂Al-400 catalysts. The total basicity of the catalysts ranged from 430–640 μ mol/g, which is shown in Table 2. The fitted desorption curves according to CO₂ desorption temperature were then displayed in Figure 6. From the results, all of the catalysts exhibited obvious bands below 250 °C and big bands from 350 to 900 °C. The peak below 250 °C could be assigned to weak basic sites of the catalysts [17,21]. However, the desorption peak of CO₂ at the higher temperature would have resulted from the medium-strength basic sites (250–470 °C), strong basic sites (470–650 °C) and super strong basic sites (above 650 °C) [21,39]. Through quantitative analysis of the basic sites, the gold catalysts supported on Zn₂Al-400 possess more strong basic sites (470–650 $^{\circ}$ C) than that on the $Zn_3Al-400$ and $Zn_1Al-400$. While using Au_{25} clusters as the precursor of gold, more super-strong basic sites (above 650 $^{\circ}$ C) were observed in Au₂₅/Zn_xAl-400 catalysts, which might be connected with their good catalytic performances. Moreover, to exclude the influence of decomposition of the residual hydrotalcites on the results of CO₂-TPD, the comparison experiments were conducted on $Au_{25}/Zn_xAl-400$ and Au/ZnAl-400catalysts without adsorption of CO_2 , which showed a clear absence of CO_2 desorption peak by acquiring the TCD and MS signal simultaneously (Figure S3).



Figure 6. CO_2 -TPD of supported gold catalysts: (a) $Au_{25}/Zn_3Al-400$; (b) $Au_{25}/Zn_2Al-400$; (c) $Au_{25}/Zn_1Al-400$; (d) $Au/Zn_2Al-400$.

2.5. The Active Sites and Reaction Mechanism

According to the catalytic performances on supported gold catalysts and calcined supports (Table 1), the active species were supposed to locate at the interface of gold particles and the supports, since the support itself was very hard to activate oxygen and transform the MAL to MMA (Table 1, entry 5–7). Moreover, the small gold particles were generally supposed to benefit the catalytic activity due to the abundant uncoordinated gold species over small gold particles [40,41]. On account of the XRD and TEM results, the average particle size of gold on the Au/Zn₂Al-400 catalyst (~2.8 nm, Figure 3d) was close to that of the Au₂₅/Zn₂Al-400 (~2.5 nm, Figure 3b), while the activity of it decreased dramatically from 93.1% (Table 1, entry 2) to 57.1% (Table 1, entry 4), and the TOF value reduced from 1626 h⁻¹ to 684 h⁻¹. Thus, the decreased activity might not be attributed merely to the size of gold.

Further characterization of the valence state of gold and the adsorption property of the catalysts were conducted by XPS and in situ CO DRIFT spectra. As shown in Figure 4, a strong adsorption peak of CO was observed on metallic gold over the Au₂₅/Zn_xAl-400 catalyst (Figure 4a–c), while no adsorption band of CO could be found on the DP-method-prepared Au/Zn₂Al-400 catalyst (Figure 4d). That is, the poor adsorption behavior of the Au/Zn₂Al-400 catalyst is very different from that of the Au₂₅/Zn_xAl-400, thus, lead to its poor activity. Moreover, CO₂–TPD results indicated more super-strong basic sites existed in Au₂₅/Zn_xAl-400 catalysts than that in Au/Zn₂Al-400 (Figure 6), which may facilitate the transformation of MAL to hemiacetal intermediate. Further characterization about the intrinsic origin of the performance was still needed to make it clear. In contrast, the thiolate-protected gold clusters were demonstrated useful as the precursor of gold in preparation of the good-performing gold catalysts with controllable sizes.

On the supported gold catalysts, the reaction mechanism for the oxidative esterification of MAL to MMA in the presence of molecular oxygen was generally involved with a two-step mechanism in the earlier study [17,38,42]. Based on this, herein, a postulated pathway over the Au₂₅/Zn_xAl-400 catalyst is proposed in detail in the combination of the characterization results and catalytic performances (Scheme 3). In the pathway, oxygen and methanol molecule was first approaching the interface and then interacted with gold particles and basic sites to form the adsorbed atomic oxygen and methoxy. After this, the nucleophilic attack of methoxy to the carbon of methyl acrolein forms the surface hemiacetal intermediate. Moreover, finally, with the assistant of atomic oxygen, the hemiacetal intermediate transforms to the target ester via β-H elimination. The acetal appeared as the byproduct, indicating the competing reaction of hemiacetal intermediate attacked by methoxy and adsorbed oxygen. That revealed the selectivity of MMA was probably dependent on the dissociation of oxygen on well-dispersed gold particles and/or the basic sites derived from the support.



Scheme 3. Reaction pathway of MAL with MeOH to form MMA.

2.6. Substrate Universality of the Catalyst

To examine the effect of the substrates on reactivity, a range of aldehydes and alcohols was extrapolated for one-step oxidative esterification, including isobutyl aldehyde, butyraldehyde, benzaldehyde and, etc. The results are shown in Table 3. As seen, different aldehydes could react with MeOH or ethanol on the $Au_{25}/Zn_2Al-400$ catalysts to form the corresponding esters, indicating the catalyst developed in this study had excellent substrate universality. Thereinto, better activity and selectivity were preferentially achieved over the saturated aldehyde, whereas substrates with a vinyl group or phenyl ring had comparably low activity. Based on the earlier study, the substrates with electron-donating substituents promoted the reaction. In contrast, substrates with electron-withdrawing substituents impeded the formation of ester [18].

Entry	Aldehyde	Alcohol	Product	Conversion (%)	Selectivity (%)
1		Methanol		69.4	92.0
2		Ethanol		53.9	64.4
3	, o	Methanol	° V	87.8	98.9
4	, o	Ethanol		91.2	97.9
5		Methanol		87.8	95.2
6		Ethanol	~ 0	93.6	91.9
7		Methanol		45.2	75.4
8		Ethanol	, in the second	> 32.4	90.3

Table 3. Catalytic performances of various aldehydes and alcohols to form the esters by oxidativeesterification over the Au_{25}/Zn_2Al -400 catalyst.

 $\begin{array}{l} \hline Reaction \ conditions: \ MAL/MeOH = 1/23 \ (molar \ ratio), \ V(MeOH) = 4.5 \ mL, \ catalyst: \ 0.05 \ g, \ T = 353 \ K, \ P_{O2} = 3 \ atm, \ t = 2 \ h. \end{array}$

2.7. Stability of Catalysts in Fixed Bed Reactor

Stability was one of the most important targets for industrial catalysts. Thus, the developed Au₂₅/Zn₂Al-400 catalyst was then evaluated in a fixed-bed reactor for synthesis of MMA through oxidative esterification. Preliminary, the optimization of reaction conditions was conducted over the $Au_{25}/Zn_2Al-400$ catalyst as a function of reaction temperature, gas hourly space velocity (GHSV) and liquid hourly space velocity (LHSV). Their catalytic performances as a consequence of the above factors are shown in Figure 7. Obviously, the catalytic activity and selectivity were largely affected by GHSV (Figure 7b) and LHSV (Figure 7c). In contrast, the temperature seems to make no difference in selectivity (Figure 7a). Based on such results, the reaction conditions at 353 K, 2.1 atm O₂, GHSV: 3000 h⁻¹ and LHSV: 10 h⁻¹ were designated for fixed-bed reactor from overall consideration. As seen from the stability results in Figure 7d, the selectivity of MMA over the Au₂₅/Zn₂Al-400 catalyst maintained at above 90% despite the initial drop. Though the activities decreased from ~90% to ~70% after 60 h, it tends to get a balance. Thus, the potential application of $Au_{25}/Zn_2Al-400$ catalyst for this reaction could be revealed. The same trends were also presented in $Au_{25}/Zn_3Al-400$ and $Au_{25}/Zn_1Al-400$ catalysts, in which both of the catalysts showed good stabilities in one-step oxidative esterification (Figure S4).



Figure 7. The oxidative esterification performances from MAL and methanol over Au₂₅/ZnAl-400 catalyst as a function of (**a**) Reaction temperature at 2.1 atm O₂, MAL/MeOH = 1/40 (molar ratio), catalyst: 0.5 g, GHSV: 3000 h⁻¹, LHSV: 10 h⁻¹; (**b**) gas hourly space velocity (GHSV) at 353 K, 2.1 atm O₂, MAL/MeOH = 1/40 (molar ratio), catalyst: 0.5 g, LHSV: 10 h⁻¹, and (**c**) liquid hourly space velocity (LHSV) at 353 K, 2.1 atm O₂, MAL/MeOH = 1/40 (molar ratio), catalyst: 0.5 g, GHSV: 3000 h⁻¹; (**d**) reaction time at 353 K, 2.1 atm O₂, MAL/MeOH = 1/40 (molar ratio), catalyst: 0.5 g, GHSV: 3000 h⁻¹; (**d**) reaction time at 353 K, 2.1 atm O₂, MAL/MeOH = 1/40 (molar ratio), catalyst: 0.5 g, GHSV: 3000 h⁻¹, LHSV: 10 h⁻¹.

3. Materials and Methods

3.1. Chemicals

All chemicals were used as-received and without any purification. All glassware was washed with Aqua Regia and rinsed with ethanol and ultrapure water. Ultrapure water (18.2 M Ω) was used throughout this work. Hydrogen tetrachloroaurate hydrate (HAuCl₄·3H₂O), sodium carbonate (Na₂CO₃, AR), sodium hydroxide (NaOH, AR), aluminum nitrate hydrate ((Al(NO₃)₃·9H₂O), 99 wt%) and methanol were purchased from Sinopharm Company (Beijing, China). Sodium borohydride (NaBH₄, 97 wt%) was purchased from Shanghai Lingfeng Chemical Reagent Company (Shanghai, China). Methacrolein (MAL, 95 wt%) was purchased from Shanghai Macklin Biochemical Technology Company (Shanghai, China). Methyl methacrylate (MMA, 99.5 wt%), cysteine, zinc nitrate hydrate ((Zn(NO₃)₂·6H₂O), 99 wt%) and ortho-xylene (CP) were purchased from Aladdin Industrial Corporation (Shanghai, China).

3.2. Preparation of the Supported Gold Clusters

The Zn-Al-HTs supported Au₂₅ nanoclusters catalysts were prepared as follows: 30 mg of the Au₂₅ clusters were dispersed into 20 mL of ultrapure water. Then, 2.00 g of the Zn-Al-HTs supports were added into the above suspension under vigorous stirring. About one hour later, the products were washed with ultrapure water and collected by centrifugal separation. Within the process, Zn-Al-HTs and the atomically precisely Au₂₅ nanoclusters were homemade according to our previous work [26–28].

The Zn-Al-HTs were prepared through the coprecipitation method. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (0.21, 0.14 and 0.07 mol) and Al(NO₃)₃·9H₂O (0.07 mol) with Zn-Al atomic ratios of 3, 2, 1 were mixed by adding 200 mL of ultrapure water to obtain the solution A. NaOH (0.438 mol) and Na₂CO₃ (0.113 mol) were placed into a 1000 mL beaker with 200 mL of ultrapure water to obtain the solution B. The solution A was slowly pumped into the solution B in a water bath at 70 °C. Moreover, then, the gel aged at the same temperature

for another 24 h at constant stirring. Afterward, the solid was filtered, washed, dried and ground to obtain the Zn_xAl -HT (x = 3, 2, 1).

Au₂₅ clusters were prepared by a NaOH-mediated NaBH₄ reduction method [26–28]. First, 5.0 mL of HAuCl₄ solution (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 at one time. About 5 min later, fresh sodium borohydride solution was quickly added into the above solution, followed by vigorous stirring for 3 h. Finally, the products were collected and washed with ethanol–water (V/V = 3:1) and dried by lyophilization. The obtained dried Zn-Al-HTs supported Au₂₅ nanoclusters samples were defined as Au₂₅/Zn_xAl-HT. Before the catalytic test, the samples were calcined at 673 K for 2 h, with a heating rate of 5 °C/min. The obtained catalysts were denoted as Au₂₅/Zn_xAl-400.

3.3. Preparation of Supported Gold Catalysts with DP Method

The supported gold catalyst with the same Zn-Al-mixed oxide was prepared by the traditional deposition–precipitation (DP) method. In a typical synthesis, an aqueous solution of HAuCl₄ (Au content: 25 g/L, 1 mL) was added to a 50 mL beaker. Then, certain amounts of Zn₂Al-HT powders were introduced into the solution under vigorous stirring. After this, 1 M NaOH solution was added to adjust the pH value of the suspension liquid to ~10. Then, the reaction was allowed to proceed at room temperature for 2 h. The obtained solids were washed, dried and calcined at 673 K for 2 h, with the heating rate of 5 °C/min. The catalysts produced by this method were denoted as Au/Zn₂Al-400.

3.4. Catalytic Test

Catalytic testing of synthesis of MMA by one-step oxidative esterification of MAL with methanol was carried out in a stainless-steel autoclave equipped with a pressure gauge and magnetic stirring. Before reaction, 0.396 mL of MAL (0.96 M), 0.121 mL of internal standard (ortho-xylene) and 4.5 mL of methanol were put into the vessel. Then, certain amounts of catalysts were introduced into the autoclave. After sealing, the autoclave was flushed with oxygen six times and then pressurized at 3 atm. To initiate the reaction, the reactor was heated to 353 K in a water bath without stirring until the temperature reached the specified value. After the reaction, the autoclave was put into cold water to terminate the reaction. Different substrates of aldehydes and alcohols for the synthesis of esters were conducted in similar conditions. The products and reactants were analyzed by gas chromatography/mass spectrometry (GC, Agilent 7890 A, Wilmington, NC, USA), which was equipped with an HP-5 (30 m, 0.25 mm inner diameter) capillary column.

3.5. Stability Test

The lifetime of the catalyst was performed in a stainless-steel fixed bed reactor (inner diameter, 10.0 mm; length, 660 mm) equipped with a K-type thermocouple for control of the reaction temperature and a mass flow controller for regulating the gas flow rate. The feed gas was a mixture of oxygen and nitrogen, with a volume ratio of 7/93. Prior to reaction, 0.5 g of the Au₂₅/Zn_xAl-400 catalysts were introduced in the middle of the reactor, with quartz sand placed above and below the catalyst bed to hold it in place. In a typical experiment, a reaction mixture of MAL and methanol (molar ratio: 1/40) was introduced into the system using a double plunger liquid pump. The reaction was carried out under the following conditions: 353 K, 3 MPa, liquid hourly space velocity (LHSV) = 10 h⁻¹ and gas hourly space velocity (GHSV) = 3000 h⁻¹. Before introducing of reaction mixture into the system, the temperature of the reactor was raised to a specific value. The total pressure of 3 MPa (oxygen partial pressure of 0.21 MPa) was achieved by regulating the back-pressure valve. The liquid products were analyzed by gas chromatography with a flame ionization detector (FID), which was equipped with an HP-5 capillary column.

3.6. Characterization

The actual loadings of gold, zinc and aluminum were measured with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation, Madison, WI, USA). The X-ray powder diffraction (XRD) patterns were determined on a PW3040/60 X'Pert PRO (PANalytical, Almelo, The Netherlands) diffractometer equipped with a Cu K α radiation source ($\lambda = 0.15432$ nm) operating at 40 kV and 40 mA. The N₂-physical adsorption-desorption tests were measured at 77 K using an AutoSorb-1 instrument (Boynton Beach, FL, USA). Prior to the measurements, the catalysts were treated at vacuum for 2 h at 120 °C. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a JEOL JEM-2100 F (Tokyo, Japan) microscope at 200 kV. The in situ diffuse reflectance infrared Fourier-transform spectroscopy of CO adsorption (CO-DRIFTS) were acquired with a Bruker INVENIO Fourier-transform infrared spectrometer (Karlsruhe, Germany), equipped with an MCT detector in the range of 600-4000 cm⁻¹. The X-ray photoelectron spectra (XPS) were conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Madison, WI, USA) equipped with a monochromated Al K α anode. The binding energies were calibrated for surface charging by referencing them to the energy of the C 1s peak at 285 eV. The temperature-programmed desorption of carbon dioxide (CO_2 –TPD) experiments were performed on Autochem II 2920 Instruments (Norcross, GA, USA) with a thermal conductivity detector and mass spectrometry. Prior to the analysis, about 50 mg of the catalysts were added into a *U*-type quartz tube reactor. Then the samples were heated in a flow of helium at 400 °C for 0.5 h. After the temperature decreased to 50 °C, the catalysts were saturated with CO_2 at 80 °C for 120 min. Finally, the samples were purged in helium at 50 °C for 95 min. The CO₂–TPD signal was recorded from 50 °C to 1000 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min with a cold trap.

4. Conclusions

In summary, Zn-Al-HTs supported Au₂₅ nanoclusters were designed and used as the precursors for direct oxidative esterification of MAL with methanol to form MMA. The Au₂₅/Zn_xAl-400 catalysts showed comparable better performances with higher activity and selectivity than the gold catalysts prepared by the DP method. XRD and TEM characterizations suggested that the Au₂₅/Zn_xAl-400 catalysts have good dispersion and small average particle sizes of gold. In situ CO DRIFT spectra and Au 4f XPS spectra indicated the metallic gold with strong CO adsorption property might attribute to this high activity. Moreover, the strong basic sites revealed by CO₂–TPD were said to facilitate the formation of hemiacetal intermediate, which contributes to the formation of the final product. Combined with the characterization results with catalytic performances, the active sites were supposed to locate at the interface between small gold particles and the support. Further substrate scope experiments and stability test in a fixed-bed reactor suggested the Au₂₅/Zn_xAl-400 catalysts have potential in these kinds of reactions. This work also provides a good reference for designing the gold catalyst with high activity and selectivity.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4 344/11/2/162/s1, Table S1: Summarization of catalytic performances of supported gold catalysts; Table S2: Element analysis of supported gold catalysts with various Zn/Al molar ratios; Figure S1: N₂ adsorption–desorption isotherms and pore size distributions of the supported gold catalysts; Figure S2: Chromatogram analysis of the liquid product before and after oxidative esterification between MAL and CH₃OH; Figure S3: TPD profiles of supported gold catalysts with various Zn/Al ratios for the synthesis of MMA from MAL and MeOH.

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