

Aerobic Oxidative Esterification of Benzyl Alcohol and Acetaldehyde over Gold Supported on Nanostructured Ceria–Alumina Mixed Oxides

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Au nanoparticles supported on nanostructured ceria-alumina mixed oxides (10 and 30 wt % ceria) were prepared by a deposition–precipitation method. Their properties were studied by N_2 adsorption, XRD, TEM, X-ray photoelectron spectroscopy, and UV/Vis spectroscopy under temperature-programmed reduction or oxidation. The materials catalyzed the liquid-phase aerobic oxidative esterification of benzyl alcohol and benzalde-hyde effectively and showed a much better performance than Au supported on the individual oxides. The reactions occurred

Introduction

Supported gold nanoparticles (AuNPs) have shown a remarkable catalytic activity in a large number of chemical transformations, in particular, in the oxidation of CO, alkenes, and alcohols.^[1–8] The oxidation of alcohols is one of the most important reactions in synthetic organic chemistry as the resulting carbonyl compounds are employed widely in various fields of the chemical industry. Nearly 15 years ago, Prati and co-workers re-

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	Supporting information for this article is available on the WWW under
(10000)	http://dx.doi.org/10.1002/cctc.201402923.

ChemCatChem 0000, 00, 0 – 0 Wiley Online Library

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with high turnover numbers (up to 19000) in methanol solutions in the absence of any auxiliary base and gave mainly methyl benzoate. The strong synergetic effect of ceria and alumina can be explained by the enhanced oxygen storage capacity of the materials prepared from mixed oxides compared to that of pure alumina and ceria. The order of the catalytic activity (Au/Al₂O₃ < Au/CeO₂ < Au/Ce(10)-Al < Au/Ce(30)-Al) correlated well with the oxygen activation capacity of the materials.

ported that supported AuNPs were effective catalysts for the oxidation of polyols by O_2 .^[9,10] Since then, a great number of studies on the aerobic oxidation of alcohols over AuNPs has been published.^[11–23] If these reactions are performed in methanol solutions, which is rather inert to aerobic oxidation, methyl esters can be obtained as final products from the oxidative esterification of alcohols.^[23–33]

Methyl esters have found practical use as solvents, diluents, extractants, and flavoring agents and are also useful intermediates for further transformations. Their syntheses usually involve two-step procedures that consist of the production of carboxylic acids or their derivatives followed by the esterification step. Only a few catalysts able to promote the direct conversion of alcohols into methyl esters using O₂ as the final oxidant have been reported, all of which are based on AuNPs, as far as we know.^[23-33] However, most of the Au systems reported for the oxidative esterification of alcohols require the presence of base. Among the few examples of the efficient synthesis of carboxylic esters from alcohols under neutral conditions, are the processes that use AuNPs supported on β -Ga₂O₃^[26] and MgO.^[30, 32] In both cases, it has been suggested that the nature of the support determines the catalytic efficiency of the material.

It is well known that the catalytic activity of Au catalysts depends on the nature of the support, the method of Au deposition, and the size and morphology of the AuNPs and their interaction with the support. Of the various metal oxides used to stabilize AuNPs, ceria (CeO₂) is considered to be one of the most efficient and collaborative supports in oxidation reactions because it is reducible and has an oxygen storage and release capacity.^[1,4,34] Ceria-supported Au catalysts have been used successfully in the oxidation of alcohols, and a variety of so-



phisticated approaches have been applied to the synthesis of the support to improve the catalytic performance of the Au.[11-17,34,35] Along with convenceria, nanocrystalline tional ceria,^[11, 34] synthesized ceria under supercritical conditions,[35] ceria foam,^[15] and mesoporous Mn-doped ceria^[16] have been

used to prepare Au catalysts for the aerobic oxidation of alco-

hols. Alumina is usually considered to be inert and inappropriate as a support for the preparation of active AuNPs.^[20] However, several examples of efficient alumina-supported Au catalysts for the oxidation of alcohols have been reported recently.^[19, 20, 23, 36]

In this work, the performance of AuNPs supported on binary nanostructured Ce-Al oxides in the liquid-phase aerobic oxidation of benzyl alcohol and benzaldehyde in methanol solutions under neutral conditions has been studied, for the first time as far as we know, in comparison with Au catalysts prepared on only CeO₂ or Al₂O₃. The effect of the catalyst pretreatment (reduction or oxidation) was also evaluated. It has been reported previously^[37] that AuNPs supported on Ce-Al mixed oxides show better activity in the oxidation of CO than those supported on only cerium or aluminum oxides.

Results and Discussion

Support characterization

The characteristics of the supports are summarized in Table 1. The introduction of ceria into alumina resulted in a significant increase in the BET surface area compared to that of pure alumina (N₂ adsorption-desorption isotherms are presented in Figure S1). This could be the modification of the morphology of alumina as the incorporation of ceria affected the pore structure of alumina dramatically (Figure S2). The mixed Ce-Al-O oxides presented pores with a smaller average diameter than pure alumina, which correlates with the ceria content. The ceria sample had a bimodal pore size distribution of approximately 4 and 8 nm. The size of ceria and alumina crystals was estimated from XRD data (Figure S3; details presented in

Ref. [37]). The incorporation of ceria into alumina did not affect the size of the alumina particles significantly. However, the ceria particles incorporated to alumina were much smaller than that in pure ceria. As the content of ceria in the mixed Ce-Al oxide increased, the size of the ceria particles increased.

The value of the band-gap energy (E_{qap}) for ceria depends usually on the method of

Table 1. Characteristic data for the supports.									
Sample	BET surface area [m ² g ⁻¹]	Average pore diameter [nm]	Particle size [nm]		Band-gap energy [eV]	Concentratio	Concentration of surface Lewis acid site [µmol g ⁻¹]		
			alumina	Cena		weak	medium	strong	
CeO ₂	23	4 and 8	-	41	3.55	0	10	0	
AI_2O_3	207	9	6.4	-	-	0	0	20	
Ce(10)-Al	340	12	5.5	3.2	3.51	10	10	0	
Ce(30)-AI	272	7	5.1	9.1	3.52	10	10	0	

sample preparation and the size of ceria crystals because it is related to the structural and electronic defects in the ceria structure. However, the prepared Ce(10)-Al and Ce(30)-Al oxides showed similar E_{gap} values (3.51 and 3.52 eV, respectively), which were surprisingly close to the value of bulk ceria (3.55 eV) in spite of the great difference in the size of ceria crystals in these samples (Figure S4). A plausible explanation is that the direct contact between alumina and ceria could affect the E_{gap} value because ceria in mixed oxides is mostly embedded into alumina. The incorporation of ceria into alumina did not affect the chemical state of Ce according to X-ray photoelectron (XPS) spectroscopy for the Ce 3d region (Figure S5).^[37]

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The acidity of the supports was studied by IR spectroscopy using pyridine as a probe molecule (described in detail in Ref. [36]). All characterized materials contained surface Lewis acid sites (LAS) only (Table 1). Bulk ceria showed only small amounts of LAS of a medium strength, whereas strong LAS were detected on the surface of nanostructured alumina in double the concentration of that of ceria. The addition of ceria to alumina decreased the strength of the surface Lewis acidity but not the concentration of the surface LAS, which is independent of the ceria content.

Catalyst characterization

The Au particle size and total Au content determined by TEM and inductively coupled atomic emission spectroscopy (ICP-AES), respectively, are presented in Table 2 for the preoxidized and prereduced samples. Typical TEM images are presented in Figure S6. The average AuNPs diameter depended on both the nature of the support and the catalyst pretreatment and varied within the range of 2.0-5.8 nm. The AuNPs supported on Ce-Al mixed oxides were characterized by a less uniform size distribution than those supported on the pure oxides because of

Sample	Au [wt %]	Sample pretreatment					
		O ₂	O ₂				
		XPS data	<i>d</i> _{Au} [nm]	XPS data	d_{Au} [nm]		
Au/CeO ₂	3.9	Au ⁰ (83.8; 0.7; 68)	2.9	Au ⁰ (83.7; 0.9, 70)	2.7		
		Au+(84.1; 2.04; 32)		Au ⁺ (84.1; 2.04, 30)			
Au/Al ₂ O ₃	3.4	Au ⁰ (83.8; 1.5; 100)	3.9	Au ⁰ (83.7; 1.2; 100)	2.0		
Au/Ce(10)-Al	3.0	Au ⁰ (83.6; 1.1; 100)	5.8	Au ⁰ (83.7; 1.0; 100)	3.8		
Au/Ce(30)-Al	1.9	Au ⁰ (83.6; 0.9; 100)	4.6	Au ⁰ (83.6; 1.1; 100)	3.7		

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the difference in the interaction of Au species with alumina and ceria in the course of the AuNPs formation (more details can be found in Ref. [37]). The size of the AuNPs after thermal treatment under O_2 was larger than that of the samples reduced in H_2 . However, this difference in size decreased as the ceria content in the sample increased. On the nonreducible alumina support, the size of the AuNPs varied after the different treatments, whereas the size of the AuNPs supported on reducible ceria was nearly the same in both the preoxidized and prereduced samples.

The electronic state of Au was evaluated by XPS measurements. The results described in detail previously^[37] are summarized in Table 2 and presented in Figure S7. The XPS spectra of the Au 4f region for Au/CeO₂ samples treated either in O₂ or H₂ exhibited two doublets separated by a binding energy (BE) of 3.67 eV (Au 4f_{7/2} and Au 4f_{5/2}). The doublets were attributed to the metallic and cationic Au species, and the BE values for Au 4f_{7/2} were 83.8 and 84.5 eV, respectively.^[38] Thus, even after reduction at 350 °C, some fraction of Au existed on the ceria surface in a cationic form probably because of the stabilization offered by this reducible support. However, only metallic Au species were found on Au/Al₂O₃, Au/Ce(10)-Al, and Au/Ce(30)-Al after both types of pretreatment.

The process of the AuNPs formation on the surface of ceria, alumina, and Ce–Al mixed oxides under temperature-programmed reduction and oxidation was studied by UV/Vis spectroscopy and reported in detail in our previous work^[37] (see Supporting Information and Figure S8). Analysis of the UV/Vis spectra of Au/Ce(10)-Al and Au/Ce(30)-Al indicated that metallic AuNPs may be stabilized in the mixed oxides on both alumina and ceria surface sites.

Catalytic studies

The catalytic activity of Au/Al₂O₃, Au/CeO₂ Au/Ce(10)-Al, and Au/Ce(30)-Al after two different types of pretreatment (reduction with H₂ or oxidation with O₂) was tested first in the oxidation of benzyl alcohol (1) with O_2 in a methanol solution. The results are presented in Table 3. All samples demonstrated a high efficiency in the oxidation and, particularly, in the oxidative esterification of benzyl alcohol in the absence of any auxiliary base, although they showed a different performance. The reaction resulted in two major products: benzaldehyde (2) and methyl benzoate (4; Scheme 1). The combined selectivity for these two products was 80-85% in all runs, and only small amounts of dimethyl acetal (3), benzyl benzoate (5), and benzoic acid (6) were detected. The relative amounts of the main products 2 and 4 depended on the reaction time, and 4 was the predominant product at the end of most runs. This kinetics is consistent with a two-step process that involves the oxidation of alcohol to aldehyde and the further oxidation of aldehyde to benzoic acid derivatives (Scheme 1).

Compounds **4** and **5** are formally the products of the esterification of benzoic acid with methanol and benzyl alcohol, respectively. However, within the mechanism accepted currently, their formation occurs through the dehydrogenation of the corresponding hemiacetals that are considered as key intermediates.^[11,25,26,39] The hemiacetals are suggested to be

Table 3. Oxidation of 1 in methanol solutions catalyzed by Au catalysts. ^[a]											
Run	Catalyst	Time [h]	Conversion [%]	Selectivity [%]					S _{mono/di} ^[b] [%]	TOF ^[c] [s ⁻¹]	TON ^[d]
				2	3	4	5	6			
Catalysts	pretreated in H ₂										
1	Au/Al ₂ O ₃	1	13	48	6	38	8	-	54/46	0.91	-
		10	67	43	12	36	11	-	53/47	-	2487
2	Au/CeO ₂	1	25	45	22	27	6	-	67/33	2.07	-
		10	92	31	7	53	9	-	38/62	-	4436
3	Au/Ce(10)-Al	1	39	51	7	35	7	-	58/42	6.77	-
		10	93	24	4	60	12	-	28/72	-	9998
4 ^[e]	Au/Ce(30)-Al	1	72	62	23	15	-	-	85/15	17.86	-
		10	100	20	3	66	4	6	23/76	-	15625
Catalysts	pretreated in O ₂										
5	Au/Al ₂ O ₃	1	30	49	0	36	7	8	49/51	4.08	-
		10	74	38	3	45	14	0	41/59	-	5768
6	Au/CeO ₂	1	24	48	14	30	8	-	62/38	2.10	-
		10	96	25	4	63	8	-	29/71	-	5194
7	Au/Ce(10)-Al	1	45	50	10	35	5	-	60/40	12.02	-
		10	99	26	5	52	12	5	31/69	-	16086
8	Au/Ce(30)-Al	1	78	58	21	15	2	4	79/21	23.40	-
		10	100	22	2	63	3	10	24/76	-	19130

[a] Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂). Conversion and selectivity were determined by GC; [b] Selectivity for the products of mono- and dioxidation: (2+3)/(4+5+6); [c] Initial rate of the substrate conversion (initial TOF) per mol of the surface Au atoms. The relative amount of surface Au atoms (Au dispersion) was calculated as 1.15 divided by the average diameter of Au particles; [d] TON calculated as a ratio between the amounts of products formed and the amounts of surface Au. It was considered that products **4**, **5**, and **6** were formed via products **2** and **3** and both steps were catalyzed by Au: TON = [n(2+3)+2n(4+5+6)]/n (Au), where *n* represents the amount of the indicated compound or Au in moles; [e] The catalyst was reused after this run without a significant loss of activity and selectivity.

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Scheme 1. Oxidation of 1 into 2, 3, 4, 5, and 6.

formed by the condensation of benzaldehyde formed in the first reaction step with methanol or benzyl alcohol. Small amounts of benzoic acid detected in the reaction solutions may be the result of the dehydrogenation of a hydrate formed by the interaction of the aldehyde with trace water instead of alcohols.

The kinetic curves for the reactions over the catalysts pretreated in H_2 or O_2 are shown in Figures 1 and 2, respectively. In all cases, the treatment in O_2 resulted in more active catalysts; however, the product distributions were similar for two sets of catalysts. The remarkable effect of the composition of the support on the catalytic performance of Au was observed, the general tendencies of which are similar for the prereduced and preoxidized materials.

The oxidation of benzyl alcohol in the presence of Au/Al₂O₃ occurred at 110 °C at a moderate rate that resulted in an approximately 70% conversion in 10 h to give the products of mono-oxidation (aldehyde **2** and its acetal **3**) and dioxidation (esters **4** and **5**) in comparable amounts (Table 3, runs 1 and 5). The introduction of ceria into alumina resulted in a significant and gradual increase in the substrate conversion rate, for



Figure 1. Oxidation of 1 in methanol solutions catalyzed by Au catalysts pretreated in H₂ at 350 °C: effect of the support (runs 1–4, Table 3). Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂).





Figure 2. Oxidation of 1 in methanol solutions catalyzed by Au catalysts pretreated in O₂ at 350 °C: effect of the support (runs 5–8, Table 3). Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂).

which the reactions over Au/Ce(10)-Al and Au/Ce(30)-Al were even faster than those over Au supported on pure ceria (Table 3, runs 3 and 4 vs. run 2; runs 7 and 8 vs. run 6).

The efficiency of the second reaction step, the aldehyde oxidation into benzoic acid derivatives, was much higher over Au supported on ceria or mixed oxides compared to that over pure alumina. For example, in 10 h reactions over Au/Ce(30)-Al, both prereduced and preoxidized, the products of dioxidation **4**, **5**, and **6** accounted for 76% of the mass balance at a complete substrate conversion, and **4** was a predominant product formed with a selectivity of approximately 65% (Table 3, runs 4 and 8). In these runs, the increase in ester selectivity with the reaction time can be seen clearly.

The reactions occurred with very low catalyst loadings (0.6 wt%) so that turnover numbers (TONs) reached high values of up to 19000, which reflects the high catalyst stability. The TON was calculated with respect to the amount of surface Au; that is, the fraction of Au atoms located on the surface of Au particles that are, therefore, accessible to the substrate.

The catalysts, which are solid materials insoluble in the reaction mixture, can be separated from the products by simple centrifugation or filtration. These features represent the important technological advantages of the process. The catalyst after the experiment described in run 4 in Table 3 was reused to convert another portion of the substrate without a significant loss of activity and selectivity. The inductively coupled plasma analysis showed no Ce in the solution separated from the catalyst after the reaction and very small concentrations of Al and Au (0.05 and 0.12% loss of Al and Au, respectively). To further verify the possible catalyst loss, fresh benzyl alcohol was added to the recovered supernatant and the solution was placed in the autoclave under oxidation conditions (110°C, 10 atm of O₂). No further conversion was observed, which indicated the lack of significant Au leaching to the liquid phase during the process and showed that the reaction was, therefore, truly heterogeneous.

The conversion of benzyl alcohol over the catalysts based on mixed oxides occurred much faster than over those prepared from the single oxides (Figures 1 and 2). Furthermore, if the data are expressed in terms of TONs and turnover frequen-

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Table 4. Oxidation of 2 in methanol solution catalyzed by Au catalysts. ^[a]									
Run	Catalyst	Conversion [%]	Selectivity [%]		ctivity TOF ^[b] %] [s ⁻¹]				
			4	6					
Catalysts pretreated in H ₂									
1	Au/Al ₂ O ₃	25	83	17	0.35	631			
2	Au/CeO ₂	67	94	6	0.99	1994			
3	Au/Ce(10)-Al	33	92	8	1.27	2062			
4	Au/Ce(30)-Al	65	93	7	2.48	5804			
Catalysts pretreated in O_2									
5	Au/Al ₂ O ₃	31	81	19	1.02	1520			
6	Au/CeO ₂	67	91	9	1.49	2120			
7	Au/Ce(10)-Al	50	85	15	2.00	4808			
8	Au/Ce(30)-Al	84	85	15	4.83	9130			

[a] Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂); reaction time 10 h. Conversion and selectivity were determined by GC. At the calculation of conversion, acetal **3** formed in small amounts as a result of the acetalization of benzaldehyde was considered as the unconverted substrate; [b] Initial rate of the substrate conversion (initial TOF) per mol of the surface Au. The relative amount of surface Au atoms (Au dispersion) was calculated as 1.15 divided by the average diameter of Au particles; [c] TON calculated as a ratio between the amount of products formed and the amount of surface Au.

cies (TOFs) by considering only surface Au atoms, the synergetic effect between alumina and ceria in Au/Ce(10)-Al and Au/ Ce(30)-Al becomes remarkable (Table 3). The Au/Ce(30)-Al catalyst was efficient in both steps of the tandem catalytic process and showed 3–6 times higher TONs and 6–20 times higher initial TOFs than AuNPs supported on pure alumina or ceria.

The kinetics of the product accumulation in the reaction solutions implies that the slowest step of the process is the formation of esters from the aldehyde. To clarify the effect of the support on this particular step, we have studied the oxidation of benzaldehyde with O₂ over Au/Al₂O₃, Au/CeO₂, Au/Ce(10)-Al, and Au/Ce(30)-Al (Table 4). The kinetic curves of these reactions are shown in Figures 3 and 4 for the prereduced and preoxidized samples, respectively. Indeed, all catalysts were less active in the oxidation of benzaldehyde than in the oxidation of benzyl alcohol under the same conditions. The main reaction product was methyl benzoate along with a small amount of benzoic acid.



Figure 3. Oxidation of **2** in methanol solutions catalyzed by Au catalysts pretreated in H₂ at 350 °C: effect of the support (runs 1–4, Table 4). Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂).

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For all samples, thermal pretreatment in O₂ resulted in a significant increase in the catalytic activity compared to the reduced counterparts, similar to that found in the oxidation of benzyl alcohol. The remarkable effect of the support composition on the catalytic performance of Au in the aldehyde oxidation was also observed, the general tendencies of which were similar for the prereduced and preoxidized samples. Au/CeO₂ showed a much higher activity in this reaction as compared to Au/Al₂O₃, which converted only 25 and 31% of benzaldehyde in 10 h (Table 4, runs 1 and 5 vs. runs 2 and 6). The introduction of ceria into alumina enhanced the efficiency of the material gradually in the oxidation of aldehyde. The substrate consumption rate over Au/Ce(30)-Al was as high as that over Au/CeO₂ or even higher (Figures 3 and 4). The presentation of the results in terms of TONs and initial TOFs illustrates the remarkable synergetic effect between alumina and ceria on the performance of AuNPs in the oxidative esterification of benzaldehyde. The Au/Ce(30)-Al catalyst showed 3-9 times higher TONs and 3-8 times higher initial TOFs than AuNPs supported on pure alumina or ceria.

The materials were tested in the oxidation of a secondary benzylic alcohol, 1-phenyl-1-propanol, to give ethyl phenyl ketone. The reactions were performed under conditions similar to those used for the oxidation of benzyl alcohol but at a lower temperature because of the higher reactivity of the secondary alcohol (substrate, 2.5 mmol; catalyst, 10 mg; methanol, 3 mL; reaction time 2 h; $100 \degree$ C; 10 atm of O₂). The order of catalytic activities in the oxidation of 1-phenyl-1-propanol: Au/Al₂O₃ (758/2550) < Au/CeO₂ (1756/2152) < Au/Ce(10)-Al (2500/6154) < Au/Ce(30)-Al (6339/8261), showed the same tendencies, which confirms the strong synergetic effect of ceria and alumina and the beneficial influence of the catalyst pretreatment in O2. TONs achieved in 2 h reactions calculated with respect to the amount of surface Au for the catalysts pretreated in H_2 and O_2 , respectively, are given in parenthesis.

The order of the catalytic activity: $Au/Al_2O_3\!<\!Au/CeO_2\!<\!Au/Ce(10)\text{-}Al\!<\!Au/Ce(30)\text{-}Al$, correlates well with the oxygen acti-



Figure 4. Oxidation of **2** in methanol solutions catalyzed by Au catalysts pretreated in O₂ at 350 °C: effect of the support (runs 5–8, Table 4). Conditions: catalyst (10 mg); substrate (2.5 mmol); methanol (3 mL); 110 °C; 10 atm (O₂).



vation capacity of the materials determined in our previous work:^[37] zero for Au/Al₂O₃, 0.18 mol₀mol_{Au}⁻¹ for Au/CeO₂, 0.48 mol₀mol_{Au}⁻¹ for Au/Ce(10)-Al, and 0.68 mol₀mol_{Au}⁻¹ for Au/Ce(30)-Al (details are presented in the Supporting Information and Figure S9). The amount of adsorbed oxygen may be considered as the measure of the relative content of (Au–ceria vacancy) active sites on the catalyst surface.

Within the mechanism accepted currently for the oxidative esterification of primary alcohols, the first reaction step involves the dehydrogenation of the alcohol into the aldehyde followed by the formation of a hemiacetal from the aldehyde and alcohol.^[11, 25, 26, 39] Finally, the dehydrogenation of the hemiacetal gives the ester. Thus, the introduction of ceria into alumina facilitates the oxygen activation to improve the performance of AuNPs in these oxidation processes because of the better accessibility of active oxygen species in the Au-ceria interfacial area. A specific Au-ceria interaction results in the increase in oxygen mobility,^[40] which can also contribute to the enhanced activity of materials that contain Au supported on ceria compared to that on alumina. The negative effect of the catalyst pretreatment in H_2 can be explained, at least for the ceria-containing materials, by the partial reduction of ceria, which could affect the capacity of the material to oxygen activation by increasing the O-support bonding energy.

Conclusions

Au nanoparticles supported on the Ce-Al mixed oxides prepared by a sol-gel technique are more active in the liquidphase aerobic oxidative esterification of benzyl alcohol and benzaldehyde than Au supported on single cerium or aluminum oxides. The reactions occur in methanol solutions in the absence of any auxiliary base and give methyl benzoate as the main product. High turnover numbers of up to 19000 reflect the high stability of the catalysts, which can be reused. The thermal pretreatment in O₂ resulted in more active catalysts than pretreatment in H₂; however, the product distributions were similar for the two sets of catalysts. The remarkable synergetic effect between ceria and alumina may be explained by the enhanced oxygen storage capacity of the materials prepared from mixed oxides compared to neat alumina and ceria. The order of the catalytic activity $(Au/Al_2O_3 < Au/CeO_2 < Au/$ Ce(10)-AI < Au/Ce(30)-AI) correlates well with the results of the oxygen activation capacity of the materials. Thus, the introduction of ceria into alumina facilitates oxygen activation by Au nanoparticles and improves their performance in the oxidation processes strongly.

Experimental Section

Catalyst preparation

Nanostructured Ce–Al mixed oxides with different contents of ceria (10 and 30 wt%) were prepared by a sol–gel method using organometallic precursors as described previously.^[41] A solution of cerium(III) 2,4-pentanedionate hydrate (Alfa-Aesar) in ethanol with moderate agitation was added to a mixture of aluminum sec-but-oxide (Alfa-Aesar) in 2-methyl-2,4-pentanediol (Alfa-Aesar), and the

mixture was heated to reflux with moderate agitation for 3 h. Hydrolysis was performed by the addition of the deionized water. The gel obtained was aged for 10 h. The samples were dried under vacuum ($\approx 10^{-3}$ torr) at 100 °C for 12 h then heated to 450 °C under N₂ and kept at this temperature for 12 h. Finally, the samples were treated in O₂ at 650 °C for 4 h for the decomposition of organic residuals. Nanostructured alumina was prepared by the same sol–gel method described above without the addition of the cerium compound. Commercial CeO₂ (Alfa-Aesar) was used as a support as well. The mixed oxide supports were encoded as Ce(X)-Al and Au/Ce(X)-Al, respectively, in which X (10 or 30) indicates the ceria content (10 or 30 wt%).

Au (calculated as 3 wt%) was supported by deposition-precipitation using urea as a precipitation agent according to the procedure developed in Ref. [37]. The support (4.0 g) was added to an aqueous solution (400 mL) of HAuCl₄ (1.6×10^{-3} M) and urea (0.42 M). The initial pH of the solution was ≈ 2 . The suspension was stirred intensively at 80 °C for 4 h and then filtered. The solid material was washed with ammonium hydroxide (25.0 M) for 30 min. Then samples were washed with water until pH 7, filtered, and dried at RT for 24 h. Finally, samples were treated in H₂ or O₂ with a continuous temperature increase from 50–350 °C with a ramp rate of 20 °C min⁻¹. The resulting materials were used in the catalytic tests.

Catalyst characterization

The chemical composition of the Au samples was determined by ICP-AES by using a Varian Liberty 110 ICP Emission Spectrometer. In a typical procedure, the sample (30 mg) was dissolved in a mixture of concentrated H_2SO_4 , HCI, and HNO₃ (20 mL, H_2SO_4 /HCI/ HNO₃ = 6:6:3, v/v) and heated to 150 °C.

Specific surface areas were determined using the BET method by N₂ thermal adsorption measurements by using a Gemini 2600 Micromeritics instrument. Before the analysis, samples were heated in an Ar flow at 350 °C for 1 h. The pore distribution was evaluated using N₂ adsorption by using a TriStar II Micromeritics unit. Before the analysis, samples were heated under vacuum at 350 °C for 12 h to eliminate support impurities and traces of adsorbed water.

The qualitative and quantitative analysis of the acid sites in the supports was performed by IR spectroscopy using pyridine as a probe molecule as described in detail previously.^[36,42] The adsorption of pyridine and the measurement of FTIR spectra were performed at 100 °C. The pyridine desorbed at 250, 350, and 450 °C corresponds to weak, medium, and strong acid sites, respective-ly.^[42] Spectral bands at $\tilde{\nu} = 1545$ and 1450 cm⁻¹, which correspond to Brønsted and Lewis acid sites, respectively, were analyzed.

TEM was performed by using a JEOL 2010 microscope. The sample was dispersed in isopropanol and dropped onto a copper grid coated with a carbon film. To determine the mean diameter of Au particles, more than 150 particles were chosen. UV/Visible diffuse reflectance spectra (UV/Vis DRS) were recorded at RT by using a Varian Cary 300 scan spectrophotometer equipped with a standard diffuse reflectance unit as described previously.^[37] XPS measurements were performed by using a Kratos AXIS 165 spectrometer using monochromatic AIK_{α} radiation ($h\nu$ = 1486.58 eV) and a fixed analyzer pass energy of 20 eV. All measured BEs refer to the C 1s line of adventitious carbon at BE = 284.8 eV. Spectrum deconvolution was performed with background estimation using the Shirley algorithm.^[43] XRD analysis was performed by using a Philips

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X'pert diffractometer equipped with a curved graphite monochromator to apply CuK_{α} (λ = 0.154 nm) radiation.

Catalytic oxidation experiments

The experiments were performed in a homemade stainless-steel reactor equipped with a magnetic stirrer. In a typical run, a mixture of the substrate (2.5 mmol), solvent (3 mL), and the catalyst (10 mg; 0.9–2.0 μ mol of Au) was transferred to the reactor. The reactor was pressurized with O_{2} to the total pressure of 10 atm and placed in an oil bath; then the solution was stirred intensively at 110°C for the reported time. The reactions were followed by GC (Shimadzu 17 instrument fitted with a Carbowax 20м capillary column and a flame ionization detector). At appropriate time intervals, stirring was stopped and, after catalyst settling, aliquots were taken and analyzed by GC. The nature of the products was confirmed by GC-MS (Shimadzu QP2010-PLUS instrument operating at 70 eV). The content of Au, Ce, and Al in the liquid phase after the reaction was measured by using a Spectro Ciros^{CCD} ICP (inductively coupled plasma) optical emission spectrometer. Deionized (DI) water (MILLI-Q) was used to prepare the solutions. The organic media was evaporated before the sample digestion, which was performed in HNO3 heated to reflux for 3 h. The volume of the samples was adjusted to 10 mL using DI water.

Acknowledgement

The authors thank Dr. Eric Flores, Francizco Ruiz, Eloiza Aparicio, MSc Pedro Casillas, Dr. Victor Garcia, and Juan Peralta for technical support. This project was supported by CONACyT (Mexico) and DGAPA-PAPIIT (UNAM, Mexico) through the grants 179619 and 203813, respectively, and by CNPq, CAPES, FAPEMIG, and INCT-Catálise (Brazil). This work is in part funded by the Irish Government under the Programme for Research in Third-Level Institutions (PRTLI) Cycle 5 and co-funded under the European Regional Development Fund.

Keywords: alcohols • gold • oxidation • oxygen • supported catalysts

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Received: November 18, 2014 Published online on ■■ ■, 0000

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FULL PAPERS

E. Smolentseva, V. V. Costa, R. F. Cotta, O. Simakova, S. Beloshapkin, E. V. Gusevskaya,* A. Simakov*

Aerobic Oxidative Esterification of Benzyl Alcohol and Acetaldehyde over Gold Supported on Nanostructured Ceria–Alumina Mixed Oxides



Mix it up: Au nanoparticles supported on Ce–Al mixed oxides are more active in the oxidation of benzyl alcohol and acetaldehyde than catalysts prepared from pure ceria or alumina, and the synergetic effect of the oxides on the performance of the Au correlates well with the oxygen activation capacity of the materials.