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PAPER

Support effect in the gas phase oxidation of ethanol over nanoparticulate gold catalysts†

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Twenty three kinds of metal oxides were screened as supports for Au nanoparticles (Au NPs) in the gas phase oxidation of ethanol. Mild oxidation to acetaldehyde, which is economically preferable, is catalyzed by Au NPs deposited on catalytically inert metal oxides, in particular, strongly acidic MoO₃ or weakly basic La₂O₃. Deep oxidation to acetic acid takes place over Au NPs deposited on n-type semiconductive metal oxides such as ZnO and V₂O₅, which exhibit a little catalytic activity for ethanol oxidation at 200 °C. Complete oxidation to CO₂ and H₂O preferentially takes place over p-type semiconductive metal oxides such as MnO₂ and Co₃O₄, and CeO₂ which has oxygen-storage and discharge capability. These metal oxides show catalytic activity for ethanol oxidation even at 100 °C producing mainly acetaldehyde, and their catalytic activity is noticeably enhanced in the conversion of ethanol and the selectivity to CO₂ by the deposition of Au NPs. The wide range of product tunability can be explained by the adsorption structures of ethanol and by the reactivities of oxygen species on the metal oxide supports.

Introduction

The chemical industry is gradually shifting its primary resources from petroleum towards renewable ones. Biomass-based ethanol (bioethanol) has been attracting growing interest as a fuel to blend into gasoline and as a chemical feedstock to replace ethylene. Ethanol production all over the world has continuously expanded from 2000 (6.4 million kL a year) up to now (34 million kL a year in 2008). Bioethanol is currently made from cornstarch in USA, from wheat-, barley-, and rye-starch in Europe, and from sugarcane-derived sucrose in Brazil. It can also be produced from the stalks left over from corn harvesting or from other cellulosic agricultural materials with little commercial value such as waste wood and switchgrass.¹

Ethanol can be transformed into valuable chemicals such as acetaldehyde, acetic acid, ethyl acetate, diethyl ether, and ethylene oxide. Current market prices of these derivatives in Japan motivate ethanol (52 yen kg⁻¹) transformation into acetaldehyde (88 yen kg⁻¹) rather than into acetic acid (47 yen kg⁻¹).² This is probably because major industrial processes for producing acetic acid are based on the carbonylation of cheap methanol produced from synthetic gases (CO, H₂) with a Rh complex catalyst, whereas acetaldehyde needs ethylene as a source and corrosive PdCl₂-CuCl₂ as a catalyst.

Catalytic transformation of ethanol has recently been reviewed for the last ten years.³ Acetaldehyde can be selectively produced in the gas phase by dehydrogenation of ethanol over supported Cu catalysts⁴ and by oxidation with O₂ over V and Mo based oxides.^{5,6} Acetic acid can be produced in water solvent over Au catalysts supported on MgAl₂O₄⁷ or on Cu doped NiO⁸ and in the gas phase over Mo–V–Nb mixed oxides combined with TiO₂ colloids.⁹

This work explores new heterogeneous catalytic systems composed of Au for gas phase ethanol oxidation with molecular oxygen. As in other reactions Au NPs can provide a wide range of tunability depending on metal oxide supports and cover mild, deep, and complete oxidations.

Experimental

1. Catalyst preparation

Supports. The majority of metal oxide supports used were commercially available metal oxide powders: MoO₃ (Kanto Chemical, specific surface area, abbreviated as SSA, 1.9 m² g⁻¹), Al₂O₃ (Catalysis Society of Japan, JRC-ALO-2, SSA 285 m² g⁻¹), TiO₂ (Nippon Aerosil, P 25, SSA 50 m² g⁻¹), SnO₂ (Sigma-Aldrich, nanopowder, particle size <100 nm), SiO₂ (Fuji Silysia Chemical, CARiACT Q-10, SSA 300 m² g⁻¹), WO₃ (propriety material), CeO₂ (Shin-etsu Chemical, SSA 161 m² g⁻¹), and ZrO₂ (Daiichi Kigenso Kagaku Kogyo, RC-100, SSA 80–120 m² g⁻¹). In addition, the following metal oxides were prepared as supports for Au catalysts.

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(a) *ZnO and La₂O₃*. An aqueous solution of metal nitrate ($1 \times 10^{-1} \text{ M L}^{-1}$) was heated to 70 °C and poured under agitation into an aqueous solution of Na₂CO₃ (1.2 times of the stoichiometric amount, $1 \times 10^{-1} \text{ M L}^{-1}$) heated at 70 °C to obtain hydroxide or carbonate precipitate. Then the suspension was kept stirred at 70 °C for 1 h. The suspension was centrifuged and the precipitate was repeatedly washed to remove sodium and chloride ions until the pH reached a steady value of around 6. The solid precursor was filtrated and dried at 80 °C overnight and finally calcined in air at 300 °C for 4 h.

(b) *V₂O₅ and Nb₂O₅*. NH₄VO₃ (Wako Pure Chemical Industries, Co., Ltd., purity 99.0%) or C₄H₄NNbO₉·xH₂O (Sigma-Aldrich Co. Ltd., purity 99.99%) were calcined in air at 300 °C for 4 h.

(c) *MnO₂*. An aqueous solution of KMnO₄ (0.4 M L^{-1}) and NaOH (1.2 M L^{-1}) was poured into an aqueous solution of Mn(NO₃)₂ (0.6 M L^{-1}) under agitation at room temperature to obtain MnO₂ precipitate.¹⁰ Then the suspension was stirred at room temperature for 1 h. The suspension was centrifuged and the precipitate was repeatedly washed to remove potassium and sodium ions until the pH reached a steady value of around 9. The solid precursor was treated in a similar manner to those of ZnO and La₂O₃.

Gold catalysts

(a) *Coprecipitation (CP) method*. An aqueous solution of HAuCl₄ and a metal nitrate ($1 \times 10^{-1} \text{ M L}^{-1}$) was heated at 70 °C and poured into an aqueous solution of Na₂CO₃ (1.2 times of the stoichiometric amount, $1 \times 10^{-1} \text{ M L}^{-1}$) heated at 70 °C to obtain hydroxide or carbonate coprecipitate. Then the suspension was stirred at 70 °C for 1 h and was centrifuged and washed to remove chloride and sodium ions until the pH reached a steady value of around 6. The solid precursor was filtrated and dried at 80 °C overnight, and finally calcined in air at 300 °C for 4 h. The Au loading was adjusted to 5 atom% [100Au/(Au + Metal)] in the starting solutions.

(b) *Deposition precipitation (DP) method*. The pH of the aqueous solution of HAuCl₄ or Au(C₂H₈N₂)₂Cl₃¹¹ ($1 \times 10^{-3} \text{ M L}^{-1}$) was adjusted to 7 by adding aqueous NaOH solution and heated to 70 °C. Then the support was dispersed and stirred at 70 °C for 1 h. The precursor was treated in a similar manner to that for coprecipitation. The concentration in the starting solution of HAuCl₄ or Au(C₂H₈N₂)₂Cl₃ was adjusted to a Au loading of 1 wt%.

(c) *Solid grinding (SG) method*. A mixture of an organo-metallic complex (CH₃)₂Au(C₅H₇O₂) (Tri Chemical Laboratories Inc.) and supports was mechanically ground in a mortar for 20 min. The sample was calcined in air at 300 °C for 4 h or reduced in a stream of 10 vol% H₂ in N₂ at 300 °C for 2 h. The Au loading was 1 wt%.

2. Catalyst characterization

The specific surface area of catalysts was calculated by the BET method from the nitrogen adsorption isotherms obtained by using a Micromeritics Tristar (Shimadzu) apparatus.

The X-ray powder diffraction measurements were conducted by using a Rigaku RINT-TTR III diffractometer using CuKα radiation ($\lambda = 0.154056 \text{ nm}$) in the transmission mode radiation in an operating mode of 50 kV and 300 mA. Transmission electron microscopic (TEM) observations were carried out by using a JEOL JEM-3000F operating at 300 kV and a JEM-2100F operating at 200 kV.

3. Catalytic tests for gas phase oxidation of ethanol and CO oxidation

Catalytic activities were measured by a continuous-flow fixed-bed quartz reactor with an inner diameter of 6 mm. Prior to the measurements, catalyst samples were heated in an air stream at 250 °C for 30 min. The reactant gas was passed through the catalyst bed (150 mg) under a total pressure of 1 atm and at a space velocity of $20000 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ at temperatures of 100–280 °C. Ethanol solution was used as a feedstock and supplied by a plunger pump. The liquid was continuously evaporated and mixed with a feed gas (2.3% O₂ in N₂) in an evaporator heated to 180 °C. Reactant gas feed was in a molecular composition of C₂H₅OH/O₂/N₂ = 1/3/126, containing a stoichiometric amount of molecular oxygen for the complete oxidation of ethanol. The effluent gas was analyzed by using a FID gas chromatograph (GC-14A/Shimadzu, column Gaskuropack 54) and a TCD gas chromatograph (GC-8A/Shimadzu, column Porapak Q and MS-5A) equipped with an automatic gas sampling system.

Catalytic activity measurements for CO oxidation were also carried out by using a fixed-bed reactor with an inner diameter of 6 mm. A reactant feed gas containing 1 vol% CO in air was passed through a catalyst bed under the same conditions as in ethanol oxidation by using a mass flow controller. The inlet and outlet gases were analyzed with an on-line gas chromatography (GC-8A/Shimadzu, activated carbon and molecular sieve 13X were used as column packing agents) to obtain both the conversion of CO and the formation of CO₂.

Results

Characterization of catalysts

The preparation methods of Au catalysts, DP, CP and SG methods were chosen depending on the type and surface properties of metal oxide supports so that Au was mostly deposited as nanoparticles smaller than 10 nm.^{12–15} Some Au catalysts which showed interesting catalytic behavior were characterized in detail.

A Au/La₂O₃ catalyst prepared by coprecipitation (CP) was active in mild oxidation to selectively produce acetaldehyde. Our previous work showed that when Au/La(OH)₃ was prepared with a molar ratio of La/Au = 2 and by calcination at 150 °C, the mean diameter of Au particles was very small and was 1.5 nm.¹⁶ In this study the molar ratio of La/Au was 19 times higher and calcination temperature was 300 °C to transform La(OH)₃ into La₂O₃. The larger ratio of La/Au is favorable to obtain highly dispersed smaller Au particles, while the higher calcination temperature causes the aggregation of Au NPs to larger ones. The catalytic activity of this Au/La₂O₃ catalyst for CO oxidation was moderately high and provided 100%

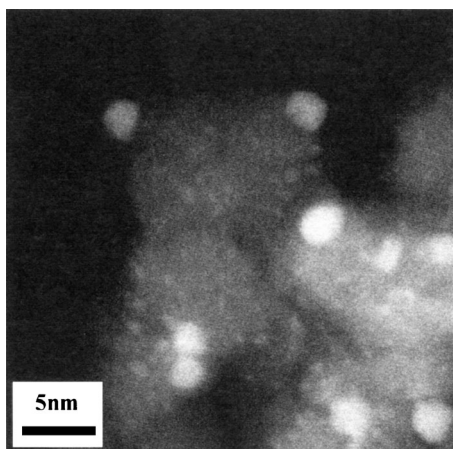


Fig. 1 TEM image of Au/ZnO prepared by CP method.

conversion of CO at 80 °C. These results suggest that Au particles were deposited on La_2O_3 as NPs below 10 nm. It was difficult to observe small Au NPs over La_2O_3 by TEM with a sharp contrast.

The TEM photograph of Au/ZnO prepared by CP is presented in Fig. 1. It contains Au NPs of a size of 3 nm and tiny Au clusters of around 1 nm. The mean diameter of Au nanoparticles was 2.6 nm.

Fig. 2 shows the XRD pattern of MnO_2 which is active for the complete oxidation without Au deposition. Although the XRD pattern was very broad, meaning low crystallinity, MnO_2 prepared by the reaction of $\text{Mn}(\text{NO}_3)_2$ with KMnO_4 in aqueous alkaline solution was identified as δ - or γ - MnO_2 , which was identical with the main phase of electrolyte manganese dioxide.

Mild oxidation of ethanol

The results of catalytic tests for Au NPs supported on 23 kinds of metal oxides are summarized in Table 1. Acetaldehyde, acetic acid, and carbon dioxide are the major products. Metal oxide supports, in principle, define the types of products. The first group leads to mild oxidation to produce acetaldehyde with high selectivities, often above 90%. The second proceeds reaction towards deep oxidation which produces both acetaldehyde and acetic acid. The selectivities to acetic acid remain at around 50%. The third group enables complete oxidation to produce CO_2 and H_2O at relatively low temperatures below 200 °C. The metal

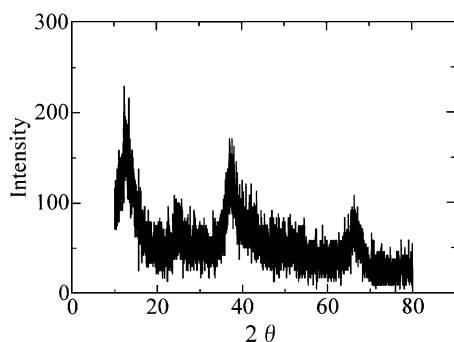


Fig. 2 XRD pattern of MnO_2 obtained by the reaction of KMnO_4 with $\text{Mn}(\text{NO}_3)_2$ in aqueous solution.

oxide supports in each group of Table 1 are listed in the order of higher main product yields at lower temperatures.

Many acidic or basic or neutral metal oxides make Au active for mild oxidation leading to the preferential formation of acetaldehyde. In particular, MoO_3 , La_2O_3 , Bi_2O_3 , SrO , and SnO_2 can provide yields higher than 50% at temperatures below 280 °C without the formation of acetic acid. Gold on La_2O_3 , Bi_2O_3 , Al_2O_3 , TiO_2 , and Y_2O_3 produces CO_2 in yields of 20–70% at temperatures above 280 °C. It is another characteristic feature that other compounds such as ethylene, acetone, ethylacetate, and diethyl ether are also byproduced at high temperatures over Al_2O_3 , Y_2O_3 , and WO_3 supports. The byproduction of these compounds can be ascribed to the surface properties of the support metal oxides as described later.

Fig. 3 and 4 show the temperature dependence of ethanol conversion and product yields over MoO_3 which is strongly acidic and over Au/ MoO_3 . Over MoO_3 without Au NPs no oxidation took place at temperatures below 200 °C but at higher temperatures acetaldehyde is gradually produced being accompanied by ethylene formation (Fig. 3). Iwasawa *et al.* reported that a SiO_2 -attached $\text{Mo}(\text{vi})$ -dimer catalyst formed acetaldehyde during ethanol oxidation.¹⁷ The deposition of Au NPs on MoO_3 shifted the temperature of oxidation toward lower temperatures by about 90 °C and markedly enhanced acetaldehyde formation. A maximum acetaldehyde yield of 94% was obtained at 240 °C (Fig. 4). The formation of

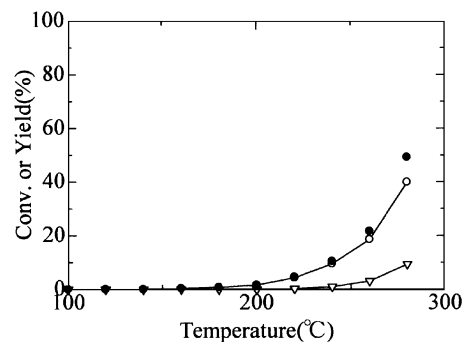


Fig. 3 Ethanol conversion (●), yields of acetaldehyde (○), ethylene (▽) as a function of reaction temperature over MoO_3 . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

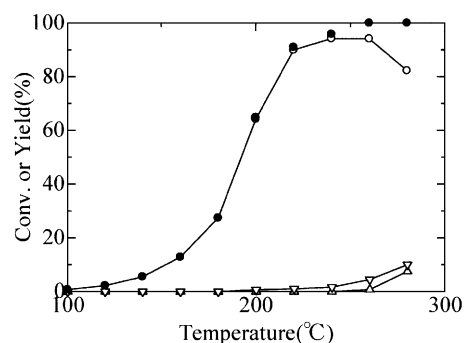


Fig. 4 Ethanol conversion (●), yields of acetaldehyde (○), acetic acid (Δ), and ethylene (▽) as a function of reaction temperature over Au/ MoO_3 . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

Table 1 Support effect on product selectivity in gas phase oxidation of ethanol over gold catalysts

Group	Support	Preparation method	Au loading/wt%	Temperature/°C	Yield (%)			
					CH ₃ CHO	CH ₃ COOH	CO ₂	Others (mainly ^a)
Mild oxidation	MoO ₃	SG	1.0	180	27	0	0	0
				240	94	0	0	5 (E)
				280	82	7	0	10 (E)
	La ₂ O ₃	CP	6.0	180	15	0	0	0
				260	81	0	0	1 (A)
				280	75	0	20	2 (A)
	Bi ₂ O ₃	CP	4.3	100	18	0	0	0
				180	68	0	0	1 (EA)
				280	8	0	72	7 (A)
	SrO	CP	9.1	100	1	0	0	0
				180	16	0	0	0
				280	67	0	0	0
	Al ₂ O ₃	DP	1.0	120	14	0	0	1 (EA)
				220	65	0	24	11 (DE)
				280	35	0	50	15 (DE)
	TiO ₂	DP	1.0	180	20	0	0	1 (EA)
				260	62	1	22	3 (EA)
				280	49	6	41	1 (EA)
	SnO ₂	DP	1.0	160	23	0	0	3 (EA)
				240	47	0	0	8 (EA)
				280	64	2	0	3 (EA)
	SiO ₂	DP	1.0	220	52	3	0	1 (EA)
				240	57	8	0	1 (EA)
				280	50	22	9	1 (EA)
	Y ₂ O ₃	CP	8.4	180	27	0	0	0
				240	57	0	9	6 (A)
				280	35	0	46	13 (A)
	MgO	CP	20.6	100	1	0	0	0
				180	6	0	0	0
				280	34	0	0	0
	Nb ₂ O ₅	SG	1.0	100	1	0	0	0
				260	30	0	0	3 (E)
				280	25	0	0	10 (E)
	BaO	CP	6.3	100	1	0	0	0
				180	8	0	0	0
				280	27	0	0	0
	WO ₃	SG	1.0	100	2	0	0	0
				180	18	0	0	36 (E)
				240	1	0	0	65 (E)
Deep oxidation	ZnO	CP	11.3	180	74	15	0	2 (EA)
				220	44	46	0	6 (EA)
				260	11	25	61	0
	In ₂ O ₃	CP	6.9	140	45	14	0	3 (EA)
				180	23	40	12	3 (EA)
				220	14	0	86	0
	V ₂ O ₅	SG	1.0	200	67	3	0	0
				240	29	36	14	21 (E)
				280	7	28	29	36 (E)
Complete oxidation	MnO ₂	DP	1.0	100	10	0	0	0
				140	9	0	79	0
				160	0	0	100	0
	CeO ₂	DP	1.0	100	22	0	0	4 (EA)
				140	49	0	14	7 (EA)
				180	0	0	100	0
	CuO	CP	11.5	100	10	0	0	0
				160	80	4	5	0
				200	0	0	100	0
	Co ₃ O ₄	CP	11.4	140	38	0	0	0
				160	3	0	41	0
				200	0	0	100	0
	NiO	CP	12.2	160	21	0	0	0
				180	18	0	27	0
				240	0	0	100	0
	ZrO ₂	DP	1.0	180	38	12	0	20 (EA)
				200	30	5	39	12 (EA)
				260	0	0	100	0
	Fe ₂ O ₃	CP	11.5	180	25	0	0	6 (EA)
				200	35	0	14	6 (EA)
				280	0	0	100	0

^a Alphabetical characters denote A = acetone, DE = diethyl ether, E = ethylene, and EA = ethyl acetate.

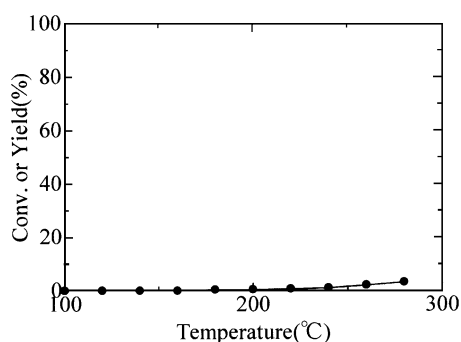


Fig. 5 Ethanol conversion (●), yields of acetaldehyde (○) as a function of reaction temperature over La_2O_3 . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$. Acetaldehyde yield was the same as ethanol conversion, meaning selectivity is 100%.

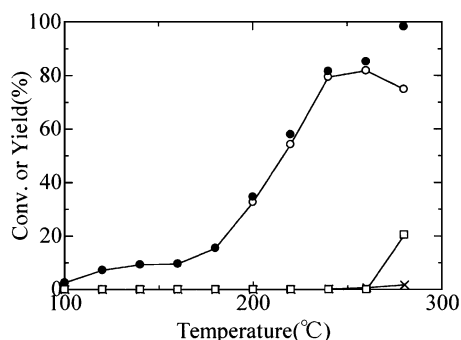


Fig. 6 Ethanol conversion (●), yields of acetaldehyde (○), CO_2 (□), and others (×) as a function of reaction temperature over $\text{Au/La}_2\text{O}_3$. Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

ethylene was observed over Au NPs deposited on acidic metal oxides (in principle, those denoted as Me_2O_3 , MeO_2 , Me_2O_5 , and MeO_3 , Me: metal) at higher temperatures. This is because acid sites promoted dehydration when reaction temperature was raised to above 180°C .

As shown in Fig. 5, La_2O_3 without Au NPs, which is weakly basic, was almost inert at and below 280°C . The deposition of Au NPs on La_2O_3 also dramatically changed the catalytic activity (Fig. 6). At temperatures above 200°C the yield of acetaldehyde remarkably increased reaching a maximum yield of 81% at 260°C without the formation of acetic acid. Above 260°C the evolution of CO_2 was observed. Other basic metal oxides (MeO: SrO , MgO , and BaO) showed similar catalytic properties; very high selectivities to acetaldehyde without byproducing ethylene and ethylacetate. The nature of the Au catalysts in this group is that the next oxidation step, formation of acetic acid, hardly takes place. The moderate reactivity of oxygen species at around 200°C and the moderate stability of surface adsorbed species of ethanol are required for the selective formation of acetic acid. The basic supports of Au catalysts firmly stabilize the surface ethoxide groups and the reactivity of oxygen species is too low to form acetic acid. Such mild oxidation capability is one of the important characteristic features of Au catalysts. It is also noteworthy that the high selectivity to acetaldehyde is characteristic to Au catalysts in gas phase oxidation and is not obtained in the oxidation in liquid water.

Deep oxidation

Deep oxidation of ethanol to form acetic acid takes place over Au NPs deposited on ZnO , In_2O_3 , and V_2O_5 , which are n-type semiconductors (Table 1). The Au catalysts of this group show high yields of acetaldehyde at temperatures below 200°C . Even at 100°C yields of acetaldehyde over 20% were obtained on Au/ZnO and $\text{Au/In}_2\text{O}_3$. With an increase in temperature the major product shifted to acetic acid and then to CO_2 . On $\text{Au/V}_2\text{O}_5$ at above 200°C ethylene yield was comparable to those of acetic acid and CO_2 . Formation of ethylene is attributed to the acidic property of the V_2O_5 support.

The best support for the deep oxidation of ethanol is ZnO which gives a high yield of acetic acid of 46% at 220°C with a selectivity of 48%. The conversion and yields for ZnO and Au/ZnO as a function of temperature are shown in Fig. 7 and 8, respectively. The ZnO support was almost inert as a catalyst at and below 280°C for ethanol oxidation (Fig. 7). The deposition of Au NPs dramatically changed the catalytic activity, giving 90% conversion at 200°C (Fig. 8). In the low temperature region ($<200^\circ\text{C}$) a main product was acetaldehyde and the highest yield of acetaldehyde was 74% at 180°C . Formation of acetic acid started at around 180°C and a maximum yield of acetic acid of 46% was obtained at 220°C . Over 250°C a main product was CO_2 . These changes in the products distribution as a function of temperature suggest that the

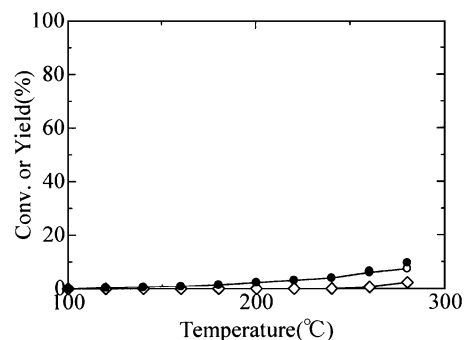


Fig. 7 Ethanol conversion (●), yields of acetaldehyde (○) and ethyl acetate (◇) as a function of reaction temperature over ZnO . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$. Acetaldehyde yield was the same as ethanol conversion up to 260°C .

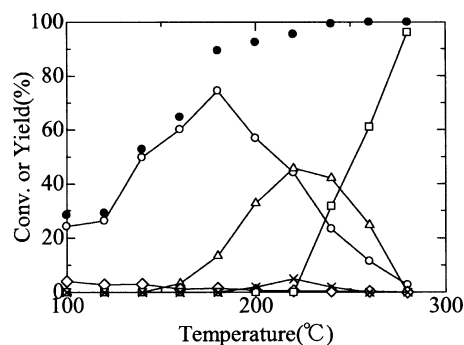


Fig. 8 Ethanol conversion (●), yields of acetaldehyde (○), acetic acid (△), ethyl acetate (◇), CO_2 (□), and others (×) as a function of reaction temperature over Au/ZnO . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

formation of acetic acid over Au/ZnO proceeds stepwise; $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COOH}$.

Christensen *et al.* reported that Au catalysts were more selective to acetic acid over 80% than Pd and Pt catalysts in liquid phase oxidation of ethanol in water as a solvent.⁷ The best performance was a selectivity of 86% to acetic acid when the conversion was 97%. Until now there is no report concerning selective acetic acid formation by the oxidation of gaseous ethanol over Au catalysts. The best supports in liquid phase oxidation (MgAl_2O_4 ⁷ and Cu-doped NiO ⁸) were not the same as those in gas phase oxidation (ZnO , In_2O_3). In the case of liquid phase oxidation water might be involved in the oxidation mechanism of ethanol.

Complete oxidation

Oxide supports which enable complete oxidation of ethanol to CO_2 and H_2O at lower temperatures are MnO_2 , CeO_2 , CuO , Co_3O_4 , NiO , ZrO_2 and Fe_2O_3 . Most of these supports are p-type semiconductors in contrast to an n-type semiconductor which is preferable for deep oxidation. Conversion and yields in ethanol oxidation over MnO_2 and Au/ MnO_2 as a function of temperature are shown in Fig. 9 and 10, respectively. Metal oxides by themselves exhibited catalytic activity at a temperature as low as 100 °C mainly producing acetaldehyde. Complete oxidation to produce CO_2 took place over 130 °C and 100% conversion of ethanol was achieved at 180 °C without formation

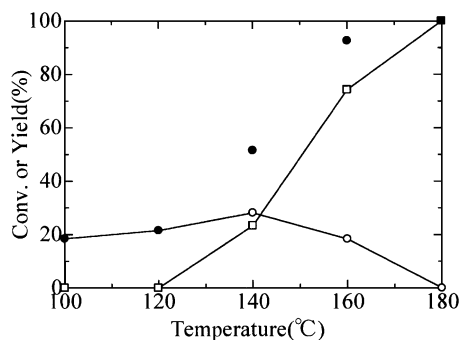


Fig. 9 Ethanol conversion (●), yields of acetaldehyde (○), and CO_2 (□) as a function of reaction temperature over MnO_2 . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

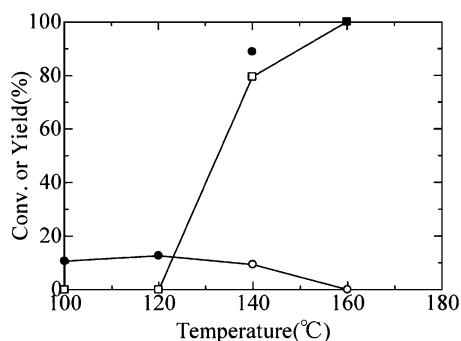


Fig. 10 Ethanol conversion (●), yields of acetaldehyde (○), and CO_2 (□) as a function of reaction temperature over Au/ MnO_2 . Reaction conditions: $\text{SV} = 20\,000\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$, $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2 = 1/3/126$.

of acetic acid (Fig. 9). This indicates that over MnO_2 the oxidation of acetaldehyde to acetic acid is slower than the oxidation of acetic acid to CO_2 at temperatures below 130 °C. Deposition of Au NPs lowers the complete oxidation temperature to reduce the yield of acetaldehyde (Fig. 10). Complete oxidation was attained at 160 °C. Apparent decrease in the yield of acetaldehyde means that acetaldehyde oxidation to CO_2 is markedly accelerated by the deposition of Au NPs. These catalysts are useful not only to decompose ethanol as one of volatile organic compounds (VOCs) in air at low temperature but also to apply to ethanol fuel cells.

Discussion

Mechanism of ethanol oxidation over supported Au catalysts

In ethanol oxidation over supported Au catalysts, the formation of surface ethoxide groups on the surfaces of metal oxide supports appears to be one of the most important processes. As shown in Fig. 11 surface ethoxide groups can be formed by the reaction of ethanol molecules with hydroxyl groups or metal cations of (a) basic metal oxide, (b) acidic metal oxide, and (c) n-type semiconductive metal oxide supports.

The next reaction step is the formation of acetaldehyde. The surface metal ethoxide is oxidized at C–H bonding to lose H to form acetaldehyde. Gold NPs deposited on metal oxides activate molecular oxygen to O_2^- or O^- depending on reaction temperature, leading to the formation of acetaldehyde.

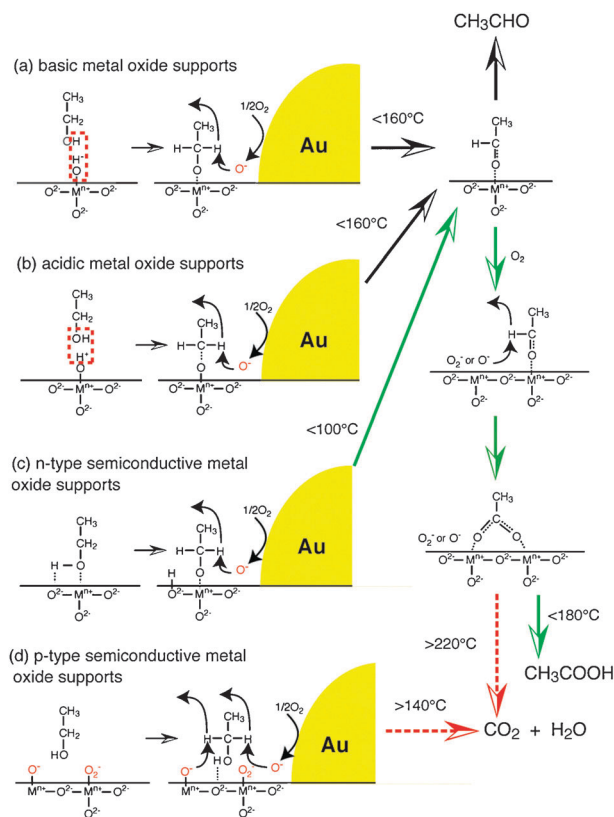


Fig. 11 Probable routes for the formation of surface ethoxide from ethanol and its transformation to acetaldehyde, acetic acid, and CO_2 over supported gold catalysts.

These active oxygen species might be formed on the corners or edges of Au NPs and at the perimeter interfaces between Au NPs and the metal oxide supports.

In the case of n-type semiconductive metal oxide supports, for example, ZnO, the third reaction step, namely the successive oxidation to acetic acid can be initiated with the active O_2^- or O^- species, which form carboxylates over the support surfaces.

In the case of p-type semiconductive metal oxide supports, which are characterized by the presence of excess surface oxygen species (O_2^- or O^-), the high population density enables the simultaneous oxidation of ethanol, acetaldehyde, acetic acid and so forth into CO_2 and H_2O . The deposition of Au NPs also promotes the formation of active oxygen species.

Conclusions

Gold catalysts are significantly tunable in the gas phase oxidation of ethanol through the selection of metal oxide supports. Gold NPs deposited on acidic or basic metal oxides can produce acetaldehyde with selectivities above 95% at temperatures above 200 °C, while Au NPs on p-type semiconductive metal oxides are active for the complete oxidation to CO_2 and H_2O at temperatures below 200 °C. Gold NPs on n-type semiconductive metal oxides produce both acetaldehyde and acetic acid. The above support effect can be explained by the stability of surface metal ethoxide and by the amount of excess surface oxygen species (O_2^- or O^-).

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