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Selective oxidation of alcohol over supported gold catalysts: methyl glycolate formation from ethylene glycol and methanol

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Abstract

An one-step selective oxidation of primary alcohol to carboxylic ester took place in liquid-phase over nano-gold particles supported on metal oxides by means of molecular oxygen. Furthermore, it was found that the oxidation of a mixture of ethylene glycol and methanol produced methyl glycolate selectively with a small amount of methyl formate. The substrate-selectivity was observed clearly with Au catalyst, not with a typical Pd or Ru catalyst, which is also capable of catalyzing the oxidative esterification of alcohol.

Keywords: Selective oxidation; Gold catalyst; Oxidative esterification

1. Introduction

Gold is rapidly recognized to be an extremely unique catalytic metal when prepared as supported nanoparticles [1]. We have been focusing on the gold-catalyzed new reactions and the industrial application, such as one-step vapor-phase oxidation of propylene to propylene oxide [2]. Recently, we have developed a new liquid-phase aerobic oxidation process for the one-step direct production of methyl glycolate (MGC) from ethylene glycol (EG) and methanol (MeOH) as starting materials by using gold-based catalysts. The process mainly consists of two parts, aerobic oxidation process and separation and purification process (Fig. 1). The product MGC is useful as chemical intermediates and monomers for various materials. Nippon Shokubai Co. Ltd. has succeeded in a pilot-scale demonstration in 2004 with a capacity of tonnes per month [3]. The key step of this process is a one-step liquid-phase air oxidation of alcohols over heterogeneous gold catalysts. The process is simple and clean continuous production systems and the product MGC is obtained with a high purity over 98%.

Nippon Shokubai's MGC process is based on the unique catalysis of nano-gold catalysts, in which gold nanoparticles supported on metal oxides can catalyze the oxidation of alcohols to the carboxylic esters with high selectivities and the oxidative esterification reveals a specific substrate-selectivity to the two reactant alcohols [4]. The main reaction scheme is shown as reaction (Scheme 1).

Although oxidative esterification of alcohols over Pd catalaysts has been already reported over 30 years ago [5], the Pd catalyst had a problem of catalyst deactivation. A gold-catalyzed selective oxidation of polyols to mono-carboxylic acid salt in alkali-aqueous medium has been reported recently in many papers [6], where the oxidation occurs highly selective but was known to take place easily over Pt catalysts. Furthermore, related papers on aerobic alcohol oxidation by Au nanoparticle catalysts have also been reported recently [7].

2. Experimental

2.1. Preparation of catalyst

Supported gold catalysts were prepared with normal deposition–precipitation method by using alkali chloroaurate solution. Metal oxides were used for the support, for example, Al_2O_3, TiO_2, ZrO_2, and others. Typical procedure of the preparation of catalyst was presented as follows for Au/Al_2O_3 (nano-Au particles supported on aluminum oxide). A 500 mL of chloroauric acid aqueous solution with a

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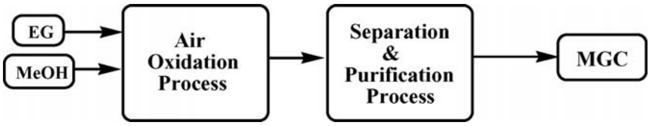

Fig. 1. Nippon Shokubai's MGC process.

$$HOCH_2CH_2OH + MeOH + O_2 \rightarrow \underset{\text{MGC (Methyl glycolate)}}{HOCH_2COOMe} + 2H_2O \quad (1)$$

$$2MeOH + O_2 \rightarrow \underset{\text{MF (Methyl formate)}}{HCOOMe} + 2H_2O \quad (2)$$

$$2HOCH_2CH_2OH + O_2 \rightarrow \underset{\text{HEGC (2-Hydroxyethyl glycolate)}}{HOCH_2COOCH_2CH_2OH} + 2H_2O \quad (3)$$

$$MeOH + HOCH_2CH_2OH + O_2 \rightarrow \underset{\text{HF (2-Hydroxyethyl formate)}}{HCOOCH_2\,CH_2OH} + 2H_2O \quad (4)$$

$$HOCH2COOMe + H_2O \rightarrow \underset{\text{GCA (Glycolic acid)}}{HOCH_2COOH} + MeOH \quad (5)$$

Scheme 1.

concentration of 10 mmol/L was kept at 65–70 °C while being adjusted to a pH of 7 with 0.5 N sodium hydroxide aqueous solution. A 40 g of powdered γ-alumina was poured into this aqueous solution under stirring, and the stirring was continued for another hour at the temperature of around 70 °C. After the supernatant was removed, the solid left was washed with water three times, and dried at 100 °C for 10 h, then calcined at 300 °C for 3 h in air. The amounts of gold in the catalyst prepared was measured by fluorescent X-ray analysis and found to be 4.6 wt.% with respect to the carrier alumina. The gold nanoparticles on the support were observed with a transmission electron microscope (TEM) and found that almost all of the particles were highly dispersed with a diameter of 5 nm or less, and the particle size distribution was narrow with a peak in the range of a particle diameter of 2–3 nm.

Au alloy catalysts were prepared by impregnating Au catalysts with a second element and then reducing with hydrogen. Pd and Ru catalysts were also prepared by a usual impregnation and a reduction treatment with hydrogen.

2.2. Reaction procedure

The oxidation of alcohols was carried out using 100 cc autoclave with rotary stirring in batch wise incorporated with a catalyst, alcohols and oxygen containing gas under the reaction conditions at 50–150 °C and 0.1–5 MPa for 1–10 h. Catalysts were used as a powder dispersed in the liquid-phase. The amount of catalyst used was 0.01–0.1 of weight ratio to the whole reaction materials. For use of two alcohols, the molar ratio of alcohol 2 to alcohol 1 was examined in the range of 5–20. The concentration of oxygen was kept at same levels as a starting period during the reaction by adding oxygen gas occasionally. After the reaction, the amount of each substrate and product were analyzed by gas chromatography.

3. Results and discussion

Typical results of alcohol oxidation over various Au catalysts are shown in Table 1. Some different types of supports were examined for Au catalysts, in which the size of Au particles was nano-meter revels. The reaction temperatures were in the range of 80–100 °C, and the reaction times were in the range from 3 to 5 h.

In case of normal mono primary alcohols, such as ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol and allyl alcohol, the main products were normal carboxylic esters, such as ethyl acetate, *n*-propyl propionate, butyl butanoate and allyl acrylate, respectively, with high selectivities over about 80% under low conversion revels. In case of diols, especially, diethylene glycol, the product was six ring lactones, 1,4-dioxanone, with high selectivity over 80%, too. In case of the reaction between two alcohols, one type of carboxylic ester was mainly produced occasionally. The reaction of methallyl alcohol and methanol produced conjugated carboxylic ester, methyl methacrylate, mainly with a high yield. Furthermore, in case of the reaction of the diols, such as ethylene glycol and 1,3-propanediol, with methanol, the products, methyl glycolate and methyl 3-hydroxy propionate, were obtained with high selectivities as main products.

Table 1
Oxidation of alcohols over various Au catalysts

Reactant		Catalyst	Temperature (°C)	Time (h)	Main product	Conversion (alcohol 1) (%)	Selectivity (main product) (%)
Alcohol 1	Alcohol 2						
Ethanol	–	Au–La–SiO_2	100	3	Ethyl acetate	18	90
n-Propanol	–	Au–TiO_2	80	5	*n*-Propyl propionate	23	81
n-Butanol	–	Au–ZrO_2	90	5	*n*-Butyl butanoate	28	79
Allyl alcohol	–	Au–ZnO	85	5	Allyl acrylate	23	76
Diethylene glycol	–	Au–Bi–TiO_2	90	4	1,4-Dioxanone	24	88
Methallyl alcohol	Methanol	Au–Pb–Al_2O_3	90	3	Methyl methacrylate	86	81
Ethylene glycol	Methanol	Au–Pb–Al_2O_3	90	3	Methyl glycolate	43	84
1,3-Propanediol	Methanol	Au–Pb–Al_2O_3	90	3	Methyl 3-hydroxypropionate	36	85

Table 2
A comparison between Au and the other metal catalysts for the reaction of EG and MeOH

Metal	Conversion (EG)	Selectivity (MGC)	Molar ratio (MF/MGC)
Au	63	83	0.24
Pd	50	54	1.63
Ru	6	76	1.26

Reaction conditions, 90 °C, 4 h; MeOH/EG = 10 (molar ratio); catalyst support, Al_2O_3; EG, ethylene glycol; MGC, methyl glycolate; MF, methyl formate.

These typical results show clearly the oxidative esterification of primary alcohols takes place easily over supported nano-gold catalysts. In addition, it was noticed that the oxidation of methanol does not take place very well compared with the oxidation of diols.

Table 2 shows the results of the oxidation of ethylene glycol (EG) and methanol (MeOH) over Au catalyst compared with the other metal catalysts, Pd and Ru, which are assumed to have a catalytically potential for the oxidative esterification of alcohols under same reaction conditions. Over Pd catalyst, MGC was formed with low selectivity and the molar ratio of methyl formate (MF) to MGC was much higher than that with Au catalyst. Over Ru catalyst, the oxidation reactivity was low and the molar ratio of MF to MGC was also higher. It has been cleared that both a high selectivity to MGC and a high substrate-selectivity to EG are obtained only with Au catalyst.

The effect of molar ratio (MeOH/EG) to the product selectivity was examined with Au catalyst under similar EG conversion revels, 62–63%. With increasing the molar ratio of MeOH to EG from 5 to 10 and 15, the selectivity to MGC also increased with 73%, 83% and 88%, while that to HEGC (2-hydroxyethyl glycolate) decreased, but the molar ratio of MF to MGC produced also increased form 0.15 to 0.24 and 0.36 (Table 3).

Table 4 shows a relationship between the substrates and the products. Four types of esters (two glycolates and two formates) can be produced theoretically. The result obtained with Au catalyst appears to be quite unique, because the formation rate of glycolates was much larger than that of formates in spite of lesser amount of EG compared with that of MeOH. The rate difference is around two orders. On the other hand, it is understandable that the difference between MGC and HEGC in total amounts of glycolates would be reflected by the difference between the concentration of MeOH and EG.

Table 3
Effect of molar ratio (MeOH to EG) for the reaction of EG and MeOH

Molar ratio (MeOH/EG)	Conversion (EG)	Selectivity		Molar ratio (MF/MGC)
		MGC	HEGC	
5	63	73	18	0.15
10	63	83	9	0.24
15	62	88	6	0.36

Reaction condition, 90 °C, 2–6 h; catalyst, Au/Al_2O_3; MGC, methyl glycolate; HEGC, 2-hydroxyethyl glycolate; MF, methyl formate.

Table 4
A relationship between the substrates and the products for use of two alcohols

Alcohol 1	Alcohol 2	
	MeOH	EG
EG	Glycolate	
	MGC	HEGC
MeOH	Formate	
	MF	HEF

MGC, methyl glycolate; HEGC, 2-hydroxyethyl glycolate; MF, methyl formate; HEF, 2-hydroxyethyl formate; $R^1CH_2OH_{\text{alcohol 1}} + R^2CH_2OH_{\text{alcohol 2}} + O_2 \rightarrow R^1COOCH_2R^2 + 2H_2O$.

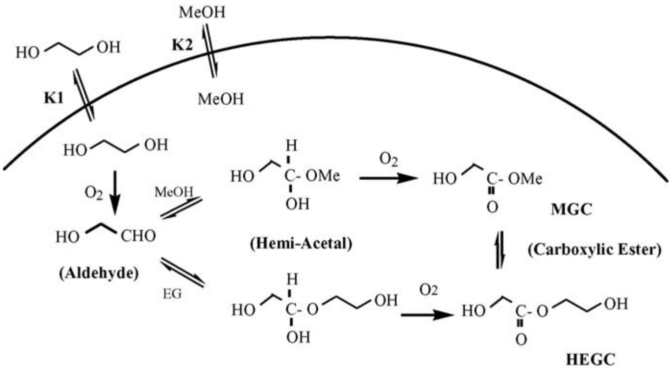

Fig. 2. A proposed mechanisms on the oxidation of ethylene glycol and methanol over nano-gold catalysts.

The study of the reaction mechanisms is underway. At present, we speculate that the reaction path is likely to be shown as below: EG → aldehyde → hemi-acetal → carboxylic ester (glycolate), and the rate-determining step could be in the first step, probably in abstraction of α-hydrogen from alcohol. We speculate, moreover, that the substrate-selectivity observed with Au catalyst is due to a competitive adsorption properties between MeOH (monodentate) and EG (bidentate) on the surface of Au particles. Supposing that the reaction takes place in Langmuir–Hinshelwood type mechanisms and the rate is in proportion on the first order to the concentration of the substrates adsorbed, the difference in the equilibrium adsorption constants could be calculated to be around two orders of magnitude based on the experimental data. It suggests that the difference in adsorption properties between two substrates on catalyst surface would be much larger on the nano-gold catalyst than on the other metal catalysts, which is the origin of the highly substrate-selectivity. Our attention is now focusing on some other selective reactions based on the hypothesis [8] (Fig. 2).

4. Conclusion

The oxidation of primary alcohols over supported nano-gold catalysts was investigated. We found that a selective oxidative esterification of primary alcohols to carboxylic esters took place with high selectivities in liquid-phase by means of molecular oxygen over nano-gold catalysts, in which the gold particles with the size of 1–5 nm were supported on metal oxides. Furthermore, it was also found that the oxidation catalysis revealed a unique substrate-selectivity, a highly selective formation of methyl glycolate (MGC) for the oxidation of a mixture of EG and MeOH. The substrate-selectivity to EG was observed clearly only with Au catalyst, not with typical Pd or Ru catalyst, which is capable of catalyzing the oxidative esterification of alcohols. We speculate this is due to the specific adsorption properties of substrates on the supported nano-gold catalyst. Based on the new and useful oxidation catalysis, Nippon Shokubai Co. Ltd. has developed a new process of MGC in pilot stage in 2004 spring.

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