Liquid phase oxidation of glycerol in flow-type reactor with molecular oxygen over highly dispersed nano-sized gold catalysts supported on Al_2O_3

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Abstract: Highly dispersed nano-sized gold including mono-atomic species supported on alumina for the oxidation of glycerol into carboxylic acids such as glyceric acid and tartronic acid were successfully prepared by deposition-precipitation (DP) method. The pHs in the DP processes affect the catalytic performances. The Au/Al_2O_3 catalyst in flow-type reactor had long-term stability and highly selectivity into target molecules. Pre-treatment by fructose as a mild reduction was very effective for the catalytic activities (initial activity and induction period) and the addition of NaOH into reactant solution was required for the glycerol oxidation over the Au/Al_2O_3 catalyst.

Keywords: Gold catalyst, Oxidation, Biomass conversion.

1. Introduction

After the grate discovery of the special catalytic performances of gold [1], the applications have been expanded not only simple reaction such as low temperature CO oxidation but also conversion of organic compounds (oxidation and hydrogenation), including biomass derived molecules, recently. Catalytic conversions of biomass are widely studied using lignocellulose, vegetable oil and so on as raw materials as well. Glycerol is one of major by-products (10% of raw material) from bio-diesel fuel process from vegetable oil and is desired to convert into high-value chemicals. Within this frame, Pagliaro *et al.* [2] summarized chemical utilizations of glycerol, and Dumaignil *et al.* [3] presented a review focused on selective oxidations of glycerol. Mimura and Dumeignil previously reported Au-Pd bimetallic catalysts prepared by ion-exchange method [4] and deposition-precipitation (DP) method [5]. Especially, ion-exchange resin was a suitable support material for liquid-phase flow reactor in that case. A continuous catalytic liquid-phase flow reaction was successfully operated using Au-Pd/anion-exchange resin over 4000 min (conversion= 50~65%, selectivity to glyceric acid= 57%, tartronic acid: 28%). There is a weak point in anion-exchange resin. Since the ion exchange resin is weak against heat (<333 K), it was difficult to increase the reaction rate by raising the reaction temperature.

In this paper, we would like to present high-performance nano-sized Au catalyst for glycerol oxidation to carboxylic acids such as glyceric acid and tartronic acid. The support material was Al_2O_3 for higher temperature reactions. The reactions were operated in liquid-phase flow reactors instead of conventional batch type reactors. The catalytic behaviors in long-term reaction were observed in continuous reactions.

2. Experimental

The nano-sized Au catalysts were prepared by conventional DP method. The powder of support material was put into pH-controlled water solution including precursor of gold ($HAuCl_4$). After the stirring for 2 h at 343 K, the precursor of the catalyst was washed by using distilled water for several times and was filtered. The separated catalyst powder was dried at room temperature for overnight and was calcined at 673 K for 4 h. The catalytic reaction tests were operated by using liquid phase flow-type reactor (EYELA, Tokyo, Japan). Catalyst was filled into the stainless-steel tubular reactor (inside diameter= 9.4 mm, length=50 mm) and there were Teflon filters at the inlet and outlet of the tube. The reaction temperatures were controlled by electric aluminum-block heater. The products were analyzed by HPLC (Shimadzu, Kyoto, Japan) with ultraviolet and refractive index detectors. The contents of Au in the catalysts were measured by inductively coupled plasma spectroscopy (ICP) technique.

3. Results and discussion

ICP results of tested Au catalysts and pHs of before and after DP methods are summarized in Table 1. In these cases, all gold precursors were not deposited on the surface of alumina supports. The pH affected the amounts of gold deposited on the surface. In the case of higher pH, the loss of gold are much compared with lower pH conditions. Therefore, operating lower pH condition could prevent loss of gold from initial amount. Results of continuous catalytic oxidation by using flow-type reactor over Au/Al_2O_3 catalysts prepared by various pH conditions are also summarized in Table 1. The main products (target products) were glyceric acid (GLYA) and tartronic acid (TA). The catalyst No. 4 indicated high selectivities into target molecules (GLYA and TA) with relatively higher conversion of glycerol.

Table 1. Properties of catalysts and results of continuous catalytic oxidation by using flow-type reactor over Au/Al_2O_3 catalysts.

No. of catalyst	Au content (ICP results) (wt %)	pH at the addition of the support and after 2 h stirring (initial pH ~ final pH after 2h)	Reaction temperature = 358 K		
			Conversion of glycerol (%)	Selectivity to glyceric acid (%)	Selectivity to tartoronic acid (%)
1	0.27	6.98 ~ 7.55	38.6	36.8	44.5
2	0.38	5.55 ~ 7.41	33.7	37.6	38.9
3	0.69	4.55 ~ 6.73	40.4	37.6	35.5
4	0.88	3.56 ~ 4.51	38.8	41.0	44.3
5	0.89	3.18 ~ 3.70	21.5	39.2	43.3

Initial amount of Au before preparation: 1.0 wt%. Properties of alumina: Specific surface area: 150 m^2/g, particle size: 50-200 μm
Reaction parameters, reactant solution: glycerol, 0.6 mol/L, NaOH, 2.4 mol/L (glycerol/NaOH=1/4 (mol/mol)),
Flow rate of reactant: 0.25 mL/min, Flow rate of oxygen: 6.0 mL/min, Catalyst weight: 0.5 g.

Figure 1 shows the long-term catalytic activity test under continuous reaction parameters. The pre-treatment (pre-reduction by fructose) at 343 K for 5h in liquid phase was very effective compared with the results using same catalyst without pre-treatment. The initial activity of pre-treated catalyst (conversion = 60%, Figure 1) was higher than that without pre-treatment (conversion = 50 %) and the conversions reached over 70 % in shorter reaction time (600min (without pre-treatment) →200 min). As the reaction without NaOH performed very low activity (1110-1410 min), NaOH is also required as the additive for the oxidation.

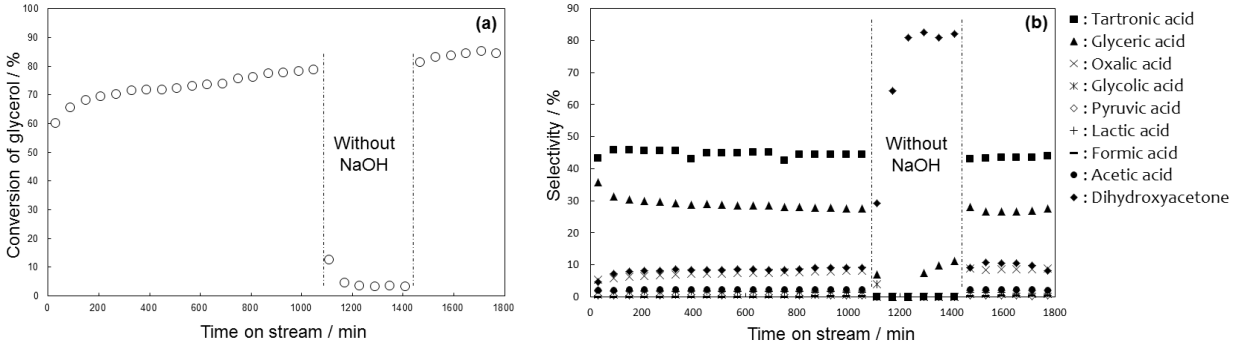

Figure 1. Long-term catalytic activity test of pre-treated (pre-reduced) Au/Al_2O_3 catalyst in flow reactor
(a) Conversion, (b) Selectivity. Pre-treatment: fructose in water, 343 K 5h in flow reactor
Catalyst: Au/Al_2O_3 (No.4 in Table 1), 2.5 g, Temperature: 343 K, Other detailed reaction parameters are same as Table 1

4. Conclusions

We successfully prepared Au/Al_2O_3 catalyst for oxidation of glycerol to carboxylic acids, such as glyceric acid and tartronic acid. In addition, we would like to show the results of detailed characterizations, such as microscope analysis, reaction kinetics and so on, on the day of our presentation.

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