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Partial oxidation of polyvalent oxygen substituted compounds on nano-scale gold catalysts

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Abstract

Investigations of the properties of supported nano-scale Au catalysts in the partial oxidation of three different polyvalent oxygen substituted compounds are presented. The relations between Au particle size and catalytic properties of Au/Al_2O_3 in the partial oxidation of ethylene glycol to glycolic acid as model reaction are discussed. Moreover, influences of the nature of the alumina support and the applied precipitation agent on the catalyst properties were studied. Furthermore, the potential of these catalysts for the industrial interesting partial oxidation of glyoxal to glyoxylic acid was checked. However, it seems that the oxidation of glyoxal is dominated by a C–C rupture leading to formic acid, mainly. Finally, the excellent selectivity of gold supported on alumina or titania in the partial oxidation of aldehyde groups of saccharides to carboxylic groups is briefly presented.

Keywords: Gold catalysts; Partial oxidation; Glycol; Glyoxal; Saccharides

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1. Introduction

Gold is a relatively new catalytic material compared to noble metals of group VIII and the other metals of group IB (Cu, Ag) of the periodic table which are extensively used in heterogeneous-catalytic processes for a long time. However, a number of interesting catalytic applications of nano-scale Au-containing materials were discovered in the last 15 years, particularly by the guiding basic work of Haruta [1]. Beside the application of such catalysts in the epoxidation of propene to propene oxide, WGS reaction, total oxidation of CO and VOC's, the partial oxidation of alcoholic and carbonyl groups to carboxylic acid functions in polyols and saccharides in liquid phase is currently a challenging task for the production of fine chemicals using renewable feedstock [2,3]. The aim of this work was to investigate and compare the catalytic properties of nano-disperse supported Au in the partial oxidation of ethylene glycol (EG), glyoxal (GO) and selected saccharides.

2. Experimental

2.1. Catalysts

Different alumina materials were used as support: Al_2O_3(P)-γ-Al_2O_3 Puralox HP14/150 (Sasol/Condea, S_{BET} = 151 m^2/g) and Al_2O_3(D)-high specific surface area Al_2O_3 prepared from ammonium dawsonite (($NH_4Al(OH)_2CO_3$), S_{BET} = 516 m^2/g) [4]. Au/Al_2O_3 catalysts were prepared by deposition/precipitation using $HAuCl_4$ and NaOH and urea, respectively, as precipitation agents. In both the cases Mg citrate was used as additive to stabilise the Au dispersity [5]. Catalyst preparation by deposition/precipitation using NaOH and reducing agents like formaldehyde and sodium formiate, respectively, was described in detail elsewhere [6]. The same procedure using NaOH was also applied for the preparation of a $0.5Au/TiO_2$ catalyst. Catalyst sample description gives Au-content (wt.%) and support. 'Homogeneous precipitation' [7] by hydrolysing urea was carried out in the following way: an aqueous solution of $HAuCl_4·3H_2O$ (450 ml) containing 900 mg chloroauric acid (2.25 mmol Au) and an excess of urea (9 g) were added to 30 g Al_2O_3 suspended in 600 ml deionised water. The mixture was stirred, heated to 70 °C

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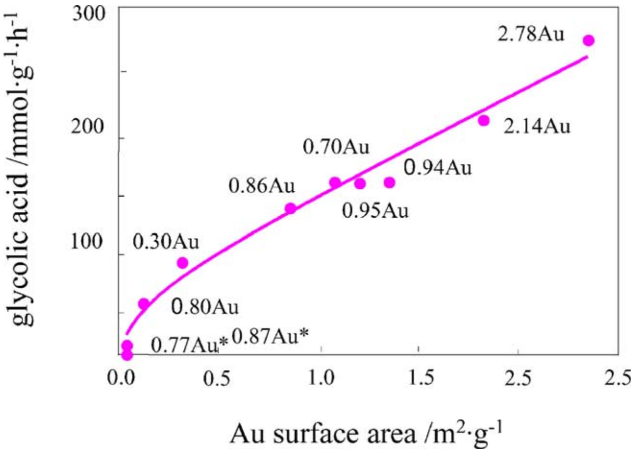

Fig. 1. Correlation between Au surface area and glycolic acid formation in oxidation of ethylene glycol on a series of Au/Al_2O_3(P) catalysts of different Au content and Au dispersity. ∗: catalyst prepared with addition of reducing agents [6].

and kept at this temperature to ensure a slow and gradual increase of the pH value by hydrolysis of urea. When a pH 6.8 was reached (70 °C; ca. 20 h) the suspension was cooled to r.t. and a Mg citrate solution (4.17 g in 90 ml water)-pre-adjusted to a pH of 7-was added. After that the suspension was additionally stirred for 1 h. The solid was separated from the liquid by centrifugation, washed free from chloride, dried under vacuum at 50 °C and calcined at 250 °C for 3 h.

2.2. *Characterisation and testing*

Au surface areas were determined by O_2-chemisorption measurements and the calculated average Au particle size was examined by TEM. The applied techniques and also the catalytic reactor used for batch tests are described elsewhere in detail [6].

First catalytic tests in EG oxidation were carried out at uncontrolled pH (examples are presented in Fig. 1 below). In order to neutralise the formed glycolic acid (GA) 0.2 mol NaOH were added to 400 ml 0.5 M EG parent solution.

Later, the tests were carried out at pH 9 fixed by pH-controlled dosing of NaOH solution (examples are presented in Table 1). The pH was lowered to 7.7 in the case of GO oxidation to prevent basic catalysed side reactions (Cannizarro dismutation). Weak basic conditions were also used for the oxidation of saccharides, e.g. glucose.

A small amount of the reaction solution was taken after various periods of time and analysed by off line-HPLC using a BioRad Aminex HPX-87H column and a 0.005 M H_2SO_4 as mobile phase for separation of the organic products.

3. Results

3.1. *Preparation influences*

Au/Al_2O_3 catalysts prepared in different ways are listed in Table 1. ICP-OES analysis revealed that only a part of the offered gold is deposited on the catalyst surface when NaOH was used as precipitating agent. Other authors also noted an incomplete deposition onto Al_2O_3 using Na_2CO_3 at pH values between 6 and 9 [7]. Higher Au loading was achieved when the ‘homogeneous precipitation’ using urea as precipitating agent was applied.

TEM investigations of the Al_2O_3(P) supported solids showed small Au particles (ca. 2 nm) in a very regular distribution when urea was used as precipitating agent. A similar particle size was found using the same support and NaOH as precipitating agent but here and there also larger Au particles (10–20 nm) were observed.

Small particles (<3 nm) in regular distribution were also detected predominately in the case of Au loading of Al_2O_3(D) using urea. However, in difference to Al_2O_3(P) relatively large Au particles (30–120 nm) were also found here and there on the support Al_2O_3(D).

3.2. *Catalytic properties*

Fig. 1 shows a correlation of GA formation on various Au/Al_2O_3(P) catalysts versus their Au surface area. GA formation was quite proportional to the Au surface area and the GA selectivity was always very high ($S > 95\%$). No significant differences were observed, i.e. no distinct change neither in activity nor selectivity was observed in a defined size range of the nano-scale Au particles. Consequently, a little growth of Au particle size observed upon a six times

Table 1
Survey on catalyst samples, their O_2 chemisorption and activity in the oxidation of ethylene glycol (EG) to glycolic acid (GA)

Samples	Precipitation agent	Au content (wt.%)	Au offered (wt.%)	$O_{2(chemis.)}$ (μmol/g)	GA formation (mmol/(g_{cat} h))[a]	GA/Au (mmol/(mg_{Au} h))
A: $0.91Au/Al_2O_3$(P)	NaOH	0.91	1.5	5.2	26.7	2.93
B: $2.78Au/Al_2O_3$(P)	NaOH	2.78	4.0	11.2	37.5	1.35
C: $1.3Au/Al_2O_3$(P)	Urea	1.30	1.5	3.8	9.1	0.70
D: $2.6Au/Al_2O_3$(P)	Urea	2.60	3.0	4.7	25.1	0.96
E: $2.6Au/Al_2O_3$(D)	Urea	2.60	3.0	17.8	66.7	2.57

EG oxidation at pH 9, $T = 76\,°C$, 400 ml of 0.5 m EG solution, EG:Au = 10,000 mol/g-atom (0.02 mg-atom Au/batch), 1 μmol $O_2 = 0.21\,m^2$ Au surface area.

[a] Initial reaction rate in the 1st hour.

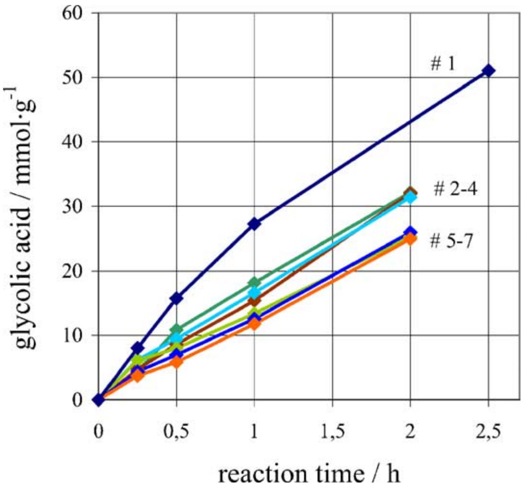

Fig. 2. Activity of catalyst $0.91Au/Al_2O_3(P)$ in ethylene glycol oxidation at pH 9 and 70 °C upon recycled use; glycolic acid formation vs. reaction time for batches 1–7.

recycling of an $Au/Al_2O_3(P)$ catalyst did not result in dramatic changes of the catalytic activity (Fig. 2). A mediate decrease and stabilising of the activity is caused by a low increase of the most frequently Au particle diameter from 2 to 2.6 nm in the first run, no gold was found in the reaction solutions after all the batches. The reason might be a leaching of very small particles ($\ll$1 nm) with a subsequent deposition on larger surface Au particles.

GA formation data obtained on various gold catalysts prepared with different alumina supports and precipitation agents are added in Table 1 in the last column. GA formation increases with the Au content in the case of preparation mode $Al_2O_3(P)$/NaOH (sample A, B) as well as $Al_2O_3(P)$/urea (sample C, D). However, significant lower specific GA formation (related to the Au content) was obtained with the samples C and D. The oxygen chemisorption was also lower on samples C and D compared to A and B, respectively. This points to a lower active gold surface area and should be one reason for the lower activity. Another reason could be a limited accessibility of Au particles deposited more inside of small pores when precipitation occurs more slowly owing to a gradual hydrolysis of urea. The latter assumption is supported by the observed higher GA formation when the high specific surface area $Al_2O_3(D)$ was loaded by gold using urea as precipitation agent (sample E), obviously the deposited gold nano-particles can be catalytically used in case of catalyst E more efficiently.

Partial oxidation of GO on Au/Al_2O_3 did not result in a useful selectivity for glyoxylic acid (GOA) as desired. Although very mild reaction conditions were used (38 °C, pH 7.7), GO:Au = 200–400 mol/g-atom) a predominate formation of formic acid (FA) was observed. For example, the molar ratio of formed GOA:FA amounted to 1.6:7.1 with a $2.75Au/Al_2O_3(P)$ catalyst. Probably, a simultaneous interaction of both aldehyde groups with the Au surface results in a C–C rupture with formation of FA. A similar observation was made by Gallezot et al. [8] for supported Ru in contrast to Pd and Pt which favour the stepwise oxidation of GO to GOA and subsequently to oxalic acid. Gallezot et al. suggested a relation between the redox potential of the platinum group metals and their selectivity in GO oxidation. Therefore, the observed undesired behaviour of Au was unexpected since the redox potential of Au is more comparable with that of Pt than that of Ru. Also the use of active carbon as support instead of alumina did not result in an improvement. A molar ratio to GOA:FA = 2.2:6.6 was obtained with a 0.35Au/C catalyst.

Partial oxidation runs using saccharide-like feed compounds showed that carboxylic groups can be generated from aldehyde groups using Au/Al_2O_3 as well as Au/TiO_2

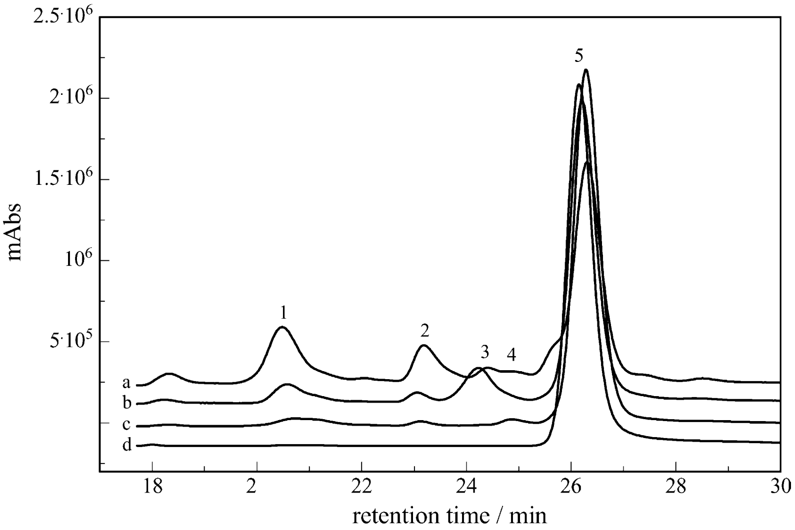

Fig. 3. Comparison of the selectivity of gold and platinum catalysts in glucose oxidation, chromatograms (UV detection) of the reaction mixture after complete conversion of 100 mmol glucose/l at pH 11 and 40 °C. Catalysts: $5Pt/Al_2O_3$ (a); 5Pt, 5Bi/C (b); $0.95Au/Al_2O_3(P)$ (c); $0.5Au/TiO_2$ (d). Products: unknown (1); glucaric and/or glucuronic acid (2); 2-keto-gluconic acid (3); 5-keto-gluconic acid (4); gluconic acid (5).

catalysts. The specific activity of the Au catalysts was significantly higher in comparison to a conventional Pt/Al_2O_3 or commercial Pt, Bi/C-catalyst. Fig. 3 demonstrates the superior selectivity of gold catalysts compared to Pt-containing systems in the oxidation of glucose to gluconic acid.

4. Conclusion

The investigations have shown that various gold amounts can be precipitated in a preferential range of a small particle size (ca. 2–5 nm) on different supports by using NaOH as well as urea as precipitating agent and Mg citrate as sticking agent. Independently from the used support, higher Au loadings were achieved when the 'homogeneous deposition' precipitation with urea was applied. The studies on the catalytic properties of the solids have shown that glycolic acid formation from ethylene glycol proportionally steady increases with the Au surface area. However, slower precipitation on a commonly used alumina using urea could lead to a covering of small pores that might be hardly accessible for reactants, i.e. lower glycolic acid formation is observed. This assumption is supported by the fact that the use of a carrier with high specific surface area leads to a significant higher glycolic acid formation, probably due to a more efficient use of the deposited gold nano-particles.

Glyoxal oxidation preferentially leads to a C–C rupture and formation of formic acid, the desired product glyoxylic acid is observed in minor only. The successful use of alumina and titania supported Au catalysts in the partial oxidation of saccharide-like reactants proofs their high potential in the production of fine chemicals from renewable sources.

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