Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 114 (2006) 369–371

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Direct synthesis of hydrogen peroxide from H_2 and O_2 using zeolite-supported Au catalysts

Gang Li [a,b], Jennifer Edwards [a], Albert F. Carley [a], Graham J. Hutchings [a,*]

[a] *Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK*
[b] *Department of Catalysis Chemistry and Engineering, Dalian University of Technology, Dalian 116012, China*

Available online 18 April 2006

Abstract

The direct synthesis of hydrogen peroxide from H_2 and O_2 using zeolite-supported Au catalysts is described and their activity is contrasted with silica- and alumina-supported Au catalysts. Two zeolites were investigated, ZSM-5 and zeolite Y. The effect of calcination of these catalysts is studied and it is found that for uncalcined catalysts high rates of hydrogen peroxide formation are observed, but these catalysts are unstable and lose Au during use. Consequently, reuse of these catalysts leads to lower rates of hydrogen peroxide formation. However, catalysts calcined at 400 °C are more stable and can be reused without loss of gold. The use of zeolites as a support for Au gives comparable rates of hydrogen peroxide formation to alumina-supported Au catalysts and higher rates when compared with silica-supported catalysts. prepared using a similar method. Zeolite Y-supported catalysts are more active than ZSM-5-supported catalysts for the stable calcined materials. It is considered that the overall activity of these supported catalysts may be related to the aluminium content as the activity increases with increasing aluminium content.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Gold catalysis; Hydrogen peroxide; Hydrogen oxidation

---

1. Introduction

The direct synthesis of hydrogen peroxide from the reaction of molecular hydrogen and oxygen has fascinated catalysis scientists for almost a century. It represents a major challenge in the control of reaction selectivity since the direct oxidation to form water, as well as the subsequent loss of hydrogen peroxide through hydrogenation or decomposition are thermodynamically favoured and are often kinetically favoured as well. Against this background it is not surprising that there is as yet no commercial process for this reaction, and industrial synthesis of hydrogen peroxide uses the sequential hydrogenation and oxidation using anthraquinone as the hydrogen carrier [1]. The direct reaction has been studied for many years and until recently the catalysts used in these investigations have been based on Pd [2–11]. However, there has been renewed interest in the direct synthesis and very recently we have shown that alumina-supported Au and Au–Pd alloy catalysts are effective for this reaction [12,13]. Haruta and co-workers have also shown that supported Au catalysts are active for this reaction and, in particular, Au/SiO_2 has been found to be the most active catalyst for the direct synthesis reaction compared with other supports in their studies [14]. In this paper we extend our earlier studies to the investigation of zeolites ZSM-5 and Y as supports and contrast the results obtained for the direct synthesis of hydrogen peroxide with alumina and silica-supported catalysts prepared using an impregnation method.

2. Experimental

2.1. Catalyst preparation

Supported catalysts were prepared using impregnation via an incipient wetness method using an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey) with nominal gold loadings of 2.5% and wt.%. For the 2.5% Au-supported catalyst the detailed procedure was as follows. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (10 ml, 5 g dissolved in water (250 ml)) was added to the support (3.8 g). Four supports were used namely, γ-alumina (Condea SCF-140), silica (Grace), zeolite HZSM-5 (Grace ZL5201, $SiO_2/Al_2O_3 = 45$, total BET surface area

---

* Corresponding author.
E-mail address: hutch@cardiff.ac.uk (G.J. Hutchings).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.070

424 m^2/g) and zeolite USY (Grace ZL5100, $SiO_2/Al_2O_3 = 6$, total BET surface area 760 m^2/g). The paste formed was ground and dried at 95 °C for 16 h and some samples were also calcined (400 °C) in static air for 3 h. Further catalysts containing different amounts of Au were also prepared using a similar procedure.

2.2. *Catalyst testing*

Hydrogen peroxide synthesis was performed using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. Typically, the autoclave was charged with catalyst (0.01 g unless otherwise stated), solvent (5.6 g MeOH and 2.9 g H_2O) purged three times with CO_2 (3 MPa) and then filled with 5% H_2/CO_2 and 25% O_2/CO_2 to give a hydrogen to oxygen ratio of 1:2, at a total pressure of 3.7 MPa at 20 °C. Stirring (1200 rpm) was started on reaching the desired temperature, and experiments were run for 30 min. Gas analysis for H_2 and O_2, was performed by gas chromatography using a thermal conductivity detector and a CP—Carboplot P7 column (25 m, 0.53 mm i.d.). Conversion of H_2 was calculated by gas analysis before and after reaction. H_2O_2 yield was determined by titration of aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ (7×10^{-3} mol/l). $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin as indicator.

The catalytic activity for CO oxidation was determined in a fixed bed quartz micro-reactor, operated at atmospheric pressure. The feed consisted of $CO/O_2/N_2$ with a molar ratio of 0.5/19.9/79.6. The combined flow rate was maintained at 22.5 ml min^{-1} and a constant catalyst loading of 50 mg was employed. The catalyst temperature was maintained at 25 °C by immersing the quartz bed in a thermostatically controlled water bath. Catalysts were tested for a minimum of 500 min and analysis of the reaction product was carried out using on-line gas chromatography. Conversion was calculated on the basis of CO_2 concentration in the effluent and carbon balances were 100 ± 2%.

3. Results and discussion

Au catalysts supported on the zeolites were prepared using impregnation and these were evaluated for the synthesis of H_2O_2 after the catalysts had been dried or calcined at 400 °C. The results are shown in Table 1. The reaction conditions we have selected have been found to be optimal in our previous studies as the use of dilute reactants at 2 °C lead to the lowest loss of hydrogen peroxide through sequential hydrogenation [12,13]. Comparable data are given in Table 1 for the synthesis of hydrogen peroxide using alumina- and silica-supported catalysts under comparable conditions. It is apparent that the zeolite-supported catalysts give comparable rates of hydrogen peroxide synthesis compared with the alumina-supported catalysts and give higher rates when compared with the silica-supported catalysts. In the previous study by Haruta and co-workers [14] silica was found to be the preferred support. In the earlier study the reaction was investigated at lower pressures but at a higher temperature of 15 °C and under these conditions the most effective catalysts were prepared by deposition and grafting methods. Indeed catalysts prepared by the relatively simple impregnation method were found to be totally inactive. Our study shows that catalysts prepared by impregnation can be active, and some of the results presented in this study are the highest yet reported for Au only supported catalysts. Interestingly, the highest rates are observed with the dried catalysts and representative data for the zeolite-supported catalysts is given in Table 1. However, these catalysts are found to leach significant amounts of Au from the catalyst and representative data are given for the zeolite Y-supported catalyst in Table 2. When the non-calcined catalysts are reused they lead to poorer catalyst performance (Table 2). Catalysts calcined at 400 °C are more stable and can be reused (Table 2).

Comparison of the calcined catalysts shows that the zeolite Y- and alumina-supported catalysts give comparable rates of hydrogen peroxide formation when measured at 30 min reaction time. The order of reactivity for these Au only catalysts is: zeolite Y–alumina ZSM-5 > silica for these initial studies. This suggests that there may be a correlation with the aluminium content of the support and we plan to investigate this in subsequent studies.

Table 1
Hydrogen peroxide synthesis and CO oxidation using catalysts prepared by impregnation

Catalyst	Preparation	Productivity (mol $H_2O_2/h/kg_{cat}$)	CO conversion (%)
2.5% Au/SiO_2	Calcined 400 °C	1.0	<1
2.5% Au/Al_2O_3	Calcined 400 °C	2.4	<1
5% Au/SiO_2	Calcined 400 °C	1.0	<1
5% Au/Al_2O_3	Calcined 400 °C	3.1	<1
2.5% Au/HZSM-5	Dried	0.5	1.2
2.5% Au/HZSM-5	Calcined 400 °C	0.69	0
4.3% Au/HZSM-5	Dried	4.73	1.7
4.3% Au/HZSM-5	Calcined 400 °C	1.75	0
2.5% Au/Y	Dried	0.95	7.7
2.5% Au/Y	Calcined 400 °C	1.02	0
4.3% Au/Y	Dried	3.61	0
4.3% Au/Y	Calcined 400 °C	2.99	0

Table 2
Leaching and reuse reactivity data for 2.5% Au/zeolite Y

2.5% Au/USY	Gold (wt.%)			H_2O_2 (mol H_2O_2/h/kg_{cat})	
	Fresh catalyst	After initial reaction	After 1st reuse	Initial reaction	First reuse
Dried	2.1	0.2	0.2	0.95	0.42
Calcined 400 °C	2.1	1.9	1.5	1.02	1.02

The data presented so far were all collected at 30 min reaction time and so the yield of hydrogen peroxide is a composite of the rates of formation and its subsequent decomposition. We therefore have investigated the effect of time of the rate of hydrogen peroxide synthesis for one of the zeolite-supported catalysts, calcined at 400 °C and the data are presented in Fig. 1.

In a subsequent set of experiments we investigated the stability of hydrogen peroxide under these reaction conditions and representative data for the zeolite Y-supported catalyst are presented in Table 3. It is clear that hydrogen peroxide is reasonably stable under these conditions particularly for short reaction times which is consistent with the data presented in Fig. 1.

In a final set of experiments we examined the activity of these supported Au catalysts for the oxidation of CO at ambient temperature and the results are given in Table 1. It is apparent that the catalysts that show enhanced activity for the direct synthesis of hydrogen peroxide are relatively inactive for the oxidation of CO. This indicates that the selective sites on the surface of the supported gold catalysts differ for these two important reactions. In our subsequent studies we will characterise these catalysts to investigate in more detail the origin of the enhanced activity for hydrogen peroxide synthesis with zeolite-supported Au catalysts.

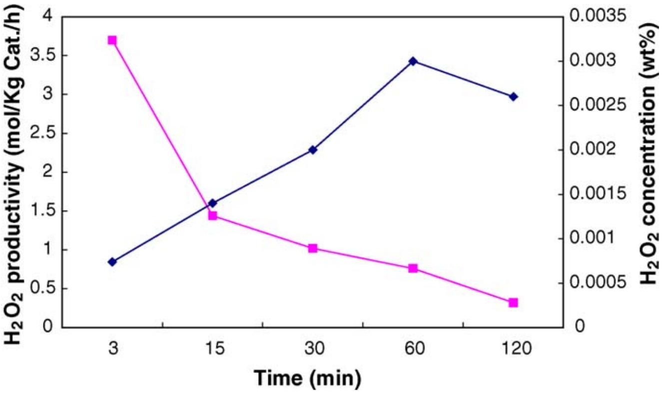

Fig. 1. Hydrogen peroxide productivity and concentration as a function of reaction time. Reaction condition: methanol 5.6 g, water 2.9 g, catalyst 2.5 wt.% Au/USY calcined 10 mg, 5% H_2/CO_2 420 psi, 5% O_2/CO_2 150 psi, temperature 0–2 °C. Key (■) H_2O_2 productivity and (◆) H_2O_2 concentration (note the scale is not linear).

Table 3
Hydrogen peroxide decomposition data on 2.5 wt.% Au/zeolite Y calcined at 400 °C

Time (min)	Hydrogen peroxide decomposition (%)
15	1.7
30	6.7
60	7.4
120	8.9

Reaction condition: methanol 5.6 g, water 2.9 g, 0.5 wt.% H_2O_2, catalyst 10 mg, 5% H_2/CO_2 420 psi, temperature 0–2 °C.

4. Conclusions

Zeolite-supported Au catalysts are effective for the direct oxidation of hydrogen to form hydrogen peroxide and give results that are comparable with alumina-supported catalysts and under our conditions are superior in performance to silica-supported catalysts prepared in the same manner using impregnation. This method of preparation is known [10,11] to lead to the formation of Au particles with mean sizes >5 nm and consequently we consider the zeolite-supported catalysts comprise Au nanoparticles decorating the surface of the zeolite crystals.

Acknowledgements

This work formed part of the EU AURICAT project (Contract HPRN-CT-2002-00174) and the EPSRC Athena project and we thank them for funding this research. We also thank the World Gold Council together with Johnson Matthey, and Cardiff University for the award of an AA Reed studentship to JKE. Gang Li thanks the China Scholarship Council (CSC) and the National Natural Science Foundation of China (No. 20406005) for the financial support to be a visiting scholar in UK.

References

[1] H.T. Hess, in: I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopaedia of Chemical Engineering, vol. 13, Wiley, New York, 1995, p. 961.
[2] L.W. Gosser, J.-A.T. Schwartz, US Patent 4,772,458 (1988).
[3] L.W. Gosser, US Patent 4,889,705 (1989).
[4] J. van Weynbergh, J.-P. Schoebrechts, J.-C. Colery, US Patent 5,447,706 (1995).
[5] S.-E. Park, J.W. Yoo, W.J. Lee, J.-S. Chang, U.K. Park, C.W. Lee, US Patent 5,972,305 (1999).
[6] G. Paparatto, R. d'Aloisio, G. De Alberti, P. Furlan, V. Arca, R. Buzzoni, L. Meda, EP Patent 0,978,316,A1 (1999).
[7] B. Zhou, L.-K. Lee, US Patent 6,168,775 (2001).
[8] M. Nystrom, J. Wanngangrd, W. Herrmann, US Patent 6,210,651 (2001).
[9] S.-E. Park, L. Huang, C.W. Lee, J.-S. Chang, Catal. Today 61 (2000) 117.
[10] E.D. Park, Y.-S. Huang, J.S. Lee, Catal. Commun. 2 (2001) 187.
[11] R. Meiers, U. Dingerdissen, W.F. Hölderich, J. Catal. 176 (1998) 376.
[12] P. Landon, P.J. Collier, A.J. Papworth, C.J. Kiely, G.J. Hutchings, Chem. Commun. (2002) 2058.
[13] P. Landon, P.J. Collier, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1917.
[14] M. Okumura, Y. Kitagawa, K. Yamagcuhi, T. Akita, S. Tsubota, M. Haruta, Chem. Lett. (2003) 822.