Catalysis Letters Vol. 101, Nos. 3–4, June 2005 (© 2005)
DOI: 10.1007/s10562-005-4886-2

Selective conversion of cyclohexane to cyclohexanol and cyclohexanone using a gold catalyst under mild conditions

Yi-Jun Xu, Philip Landon, Dan Enache, Albert F. Carley, M. W. Roberts, and Graham J. Hutchings*
School of Chemistry, Cardiff University, Cardiff, CF 10 3TB, UK

Received 3 January 2005; accepted 11 January 2005

The oxidation of cyclohexane to cyclohexanol and cyclohexanone are investigated using supported gold catalysts using mild conditions of temperature and pressure. These catalysts are found to show some limited activity at 70 °C. However, the gold catalysts do not exhibit significantly different behaviour from supported Pt or Pd catalysts, and the selectivity observed is solely a function of conversion which in turn is a function of reaction time. It is clear that at very low conversions very high selectivities can be observed, but high selectivity under these mild reaction conditions cannot be maintained at higher conversions.

KEY WORDS: oxidation; cyclohexane; gold; cyclohexanol; cyclohexanone.

1. Introduction

One of the most important recent discoveries concerning catalysis has been the discovery that gold, long considered to be an inert noble metal, is a highly reactive heterogeneous catalyst. This has led, in the last 2–3 years, to a dramatic increase in interest in catalysis by gold [1], although the first indications were made nearly two decades ago with the prediction that gold would be the most effective catalyst for acetylene hydrochlorination [2] and the seminal studies by Haruta *et al.* [3] concerning the low temperature oxidation of carbon monoxide. These early studies have now generated this new interest, in particular in the design of selective oxidation catalysts based on supported gold nanocrystals. For example, gold catalysts have been shown to be very selective for the oxidation of alcohols to acids [4–6] and we have shown that complete specificity for glycerol oxidation to glyceric acid can be observed [7,8]. In addition, gold catalysts have been shown to be highly selective for the synthesis of hydrogen peroxide from the direct oxidation of hydrogen [9,10]. Gold is therefore rapidly becoming a versatile oxidation catalyst that is capable of catalysing processes that other metals cannot achieve with such specificity.

Activation of C–H bonds in alkanes is known to be very difficult to achieve selectively at temperatures below 100 °C [11,12]. To date, the lowest temperature for selective oxidation of the alkane C–H bond has been achieved by Thomas *et al.* using transitional metal ions substituted molecular sieve catalysts at 100 °C [11–14]. We therefore wished to investigate the activation of C–H bonds at temperatures below this, and in particular we have examined the use of supported gold catalysts and we have found that they can be effective at temperature as low as 70 °C.

One of the most important alkane activation processes currently operated industrially is the oxidation of cyclohexane to cyclohexanol and cyclohexanone, which in a recent review has been acknowledged to be a reaction that continues to be a significant challenge [15]. The aerobic oxidation of cyclohexane is central to the production of nylon-6 and nylon-6,6 and the worldwide production exceeds 10^6 tonnes per annum. Commercially the process is operated at 150–160 °C with cobalt naphthenate as an initiator for the radical oxidation process that gives 70–85% selectivity at 4% conversion. Operation at high conversions leads to total oxidation and consequently this large-scale commercial process has been designed to operate at low conversion. There is clearly scope to produce a more efficient process but given the current focus on green chemistry the main scope is to design a system that gives 100% specificity. One approach has been to use hydrogen peroxide as oxidant, and promising results have been obtained with vanadium phosphate catalysts [16] and Cr-MCM-41 [17]. However, it is recognized that the desired ideal oxidant is air (or its reactive component dioxygen, O_2) and the observation of high selectivity with air has been more elusive which can be attributed to the fact that air oxidations are intrinsically non-selective and difficult to control [12,18]. Ratnasamy and co-workers [19] have shown that μ_3-oxo-bridged Co/Mn cluster complexes were very selective as homogeneous catalysts, but it is generally recognised that a heterogeneous catalyst is preferred. Recently, Nowotny *et al.* [20] have investigated immobilization of cobalt complexes but leaching occurs under reaction conditions. One of the most

---

* To whom correspondence should be addressed.
E-mail: hutch@cf.ac.uk

1011-372X/05/0600–0175/0 © 2005 Springer Science+Business Media, Inc.

significant advances in this oxidation chemistry has been the work of Thomas and co-workers [21] using aluminophosphates substituted with Mn(III), Co(III) and Fe(III) could give very high selectivities when operated at 130 °C.

Most recently, Zhao *et al.* [22,23] have shown that gold can be active for the activation of cyclohexane at 150 °C and selectivities of ca. 90% can be achieved for the Au/ZSM-5 catalyst, and >90% for a Au/MCM-41 catalyst although an initial induction period was apparent with these catalysts. It was also shown that these gold catalysts can be resused but the activity gradually declines and the selectivity shifts from cyclohexanone to cyclohexanol. These studies show that supported gold catalysts are indeed active for the activation of C–H bonds but the temperature used for these studies was 140–160 °C, which is significantly higher than the temperature range we wished to explore. We have concentrated on attempting to activate cyclohexane at temperatures well below 100 °C, using oxygen as oxidant, and in this paper we explore this for a range of supported gold catalyst.

2. Experimental methods

About 1 wt.% gold catalyst supported on graphite was prepared as follows. The carbon support (graphite, Johnson Matthey, 113.2 g) was stirred in demineralised water (1 l) for 15 min. An aqueous solution of $HAuCl_4$ (41.94% Au, Johnson Matthey, 2.38 g) in water (70 mL) was slowly added dropwise over a period of 30 min. The slurry was then refluxed for 30 min, cooled and reduced with formaldehyde over a period of 30 min. The slurry was then refluxed for 30 min and, following cooling, the catalyst was recovered by filtration and washed with water until the washings contained no chloride. The catalyst was dried for 16 h at 105 °C. This method was also used to prepare 0.25 wt.% Au/graphite and 0.5 wt.% Au/G catalyst samples using smaller amounts of chloroauric acid.

Pt and Pd catalysts supported on graphite were prepared as follows. An aqueous solution of a platinum or palladium chloride salt (5% Pt metal by weight of support) was added to the stirred carbon slurry and reduced with formaldehyde. The slurry was allowed to settle and was filtered, washed free of chloride. The catalyst was dried at 105 °C for 16 h. This method was also used to prepare a 1 wt.% Pt or Pd/graphite catalysts using smaller amounts of metal chloride.

Heterogeneously catalysed reactions in the absence of added solvent were conducted using two methods: (i) Reactions in a stirred autoclave reactor were operated by suspending the catalyst (0.12 g) in 10 mL cyclohexane in a Parr autoclave (50 mL). Radical initiator TBHP was added as required. The autoclave was pressurised to the required pressure with oxygen (3–5 bar) and heated to the temperature (70 °C). The reaction mixture was stirred (1500 rpm) for 3 h. (ii) Reactions in a stirred glass reactor were carried out using equal quantities of catalyst, cyclohexane and radical initiator in a 50 mL round-bottomed flask with reflux condenser connected. Experiments were carried out in an oil bath heated to 70 °C, with reaction mixtures stirred for the time as required.

Analysis of products in reactions was carried out using GC (Varian Star 3400 CX) fitted with DB-5 column and FID. Samples were taken at the end of reactions, 200 μL of sample was added to 20 μL of standard (3-pentanone, 98%, Aldrich) and 0.5 μL of this sample was analysed. It is essential that an internal standard is added so that the carbon mass balance can be determined to ensure that all products are observed [7]. Attempts to find a suitable internal standard that could be added prior to reaction were found to be unsuccessful as they were readily oxidized under the reaction conditions. Hence, it is necessary to add the standard immediately following the reaction as described elsewere [7].

3. Results and discussion

Our initial experiments were carried out using a range of polar and apolar solvents either using a glass reactor at ambient pressure or using an autoclave at 0.3 MPa both using air as oxidant and with a range of radical initiators with 1% Au/graphite as catalyst. We had previously shown that this catalyst was very selective for

Table 1
Cyclohexane oxidation using 1% Au/graphite in the presence of solvents

Solvent	Conversion[a] (%)	Conversion[b](%)
Methanol	65.3	82.6
Water	100	100
Toluene	0.0	0.0
p-Xylene	0.0	0.0
Cumene	15.5	0.0
Mesitylene	0.0	0.0
Acetonitrile	8.9	0.0
Quioline	0.0	0.0
Benzoyl alcohol	0.0	6.0
Acetic acid	6.5	16.5
Benzonitrile	12.5	0.0
1,2,4,5-TMB/toluene	0.0	0.0
Dioxane	0.0	0.0
THF	0.0	0.0
Chlorobenzene	0.0	0.0
1,2,3,5-TMB	0.0	0.0

[a] Reaction conditions: 70 °C, 0.012 cyclohexane, 0.22 g catalyst, 0.08 g TBHP, 20 mL solvent, 24 h, using a glass reactor.
[b] 70 °C, 0.012 mol cyclohexane, 0.22 g catalyst, 0.08 g TBHP, 3 bar O_2, 20 mL solvent, 1500 rpm, 3 h, using an autoclave reactor.
TMB: tetramethylbenzene; THF: tetrahydrofuran; no products were observed in blank experiments in the absence of catalyst.

the oxidation of glycerol in the presence of base (7,8). Although cyclohexane conversion was observed, particularly with methanol and water as solvents, no partial oxidation products were observed (table 1). However, at 70 °C when no solvent was used selective products were observed in small amounts when tertiary butyl hydroperoxide was used as an initiator (table 2). Cyclohexanol and cyclohexanone were observed as primary target products, and no adipic acid was formed. No conversion was observed in the absence of gold, i.e. using graphite alone or in the absence of catalyst but with all other reaction components present, confirming that the catalysis is intimately involved with the gold. In addition, no conversion was observed in the absence of tertiary buty hydroperoxide indicating that the supported gold nanocrystals alone could not activate dioxygen at this low temperature. No conversion was observed in the absence of dioxygen but with the gold catalyst and tertiary butyl hydroperoxide being present, showing that the hydroperoxide alone is not involved in the oxidation chemistry.

We studied the progress of the reaction with increasing time and the selectivity to partial oxidation products decreases with increasing reaction time and conversion (figure 1), when the experiments are carried out using a batch reactor. The selectivity to cyclohexanone and cyclohexanol combined are found to be highly dependent on the conversion which, in turn is a fuction of reaction time. As it was apparent that the graphite supported gold catalyst was effective at activating alkane C–H bonds in cyclohexane under mild conditions (70 °C, 0.1 MPa air) we decided to investigate the effect of a range of supported gold catalysts with different gold concentrations. The data for selectivity versus conversion at constant temperature is shown in figure 2 for data collected after 9 h reaction, and in figure 3 for data collected after 17 h reaction. As expected the selectivity observed at the longer reaction time is much lower than that at shorter reaction times, but both show the same trends, i.e. that the selectivity is dependent on conversion and is independent of the nature of the gold catalyst. In view of this we tested supported Pd and Pt catalysts and the data for these catalysts is also shown in figures 2 and 3. Interestingly, the data for the supported Pd and Pt catalysts falls on the same curves showing that gold is not particularly different from supported platinum or palladium for this reaction. Golunski and coworkers have previously made this point in another context [24].

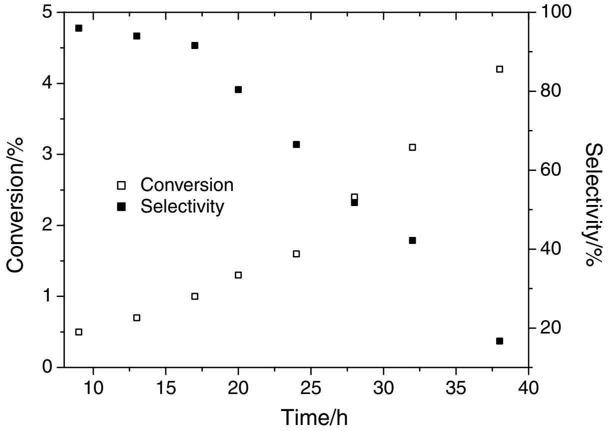

Figure 1. Time dependence of the conversion of cyclohexane and the selectivity for cyclohexanol and cyclohexanone combined using 0.5% Au/Graphite catalyst at 70 °C with standard reaction conditions.

In a recent paper, Maschmeyer and co-workers [20] have investigated the addition of chlorobenzene during the reaction. In view of this, we have examined the use of a range of additives, which is able to behave as inhibitors in our reaction system with gold catalysts, and these results are shown in table 2. At first sight it appears that 1,4-difluorobenzene gives an improvement in catalyst performance, and under some conditions very high selectivities can be achieved when the reaction proceeds for a short time. However, when these data are

Table 2
Cyclohexane oxidation without solvent[a]

Catalyst[b]	Time (h)	Additive	Conv. (%)	Selectivity (%)		
				Cyclohexanol	Cyclohexanone	Total
0.25%Au	17	–	4.7	9.5	5.8	15.3
0.5%Au	17	–	6.0	11.0	6.2	17.2
1%Au	17	–	3.7	14.4	8.7	23.1
2%Au	17	–	7.3	5.9	4.0	9.9
0.5%Au	17	1,4-difluorobenzene	1.0	48.1	43.5	91.6
0.5%Au	17	chlorobenzene	1.1	32.4	21.1	53.5
0.5%Au	17	fluorobenzene	1.1	35.7	29.0	64.7
0.5%Au	17	1,4-dichlorobenzene	1.4	32.2	20.1	52.3
0.5%Au	17	1-chloro-4-fluorobenzene	0.9	36.5	23.4	59.9
0.5%Au	17	hexafluorobenzene	1.3	25.4	15.2	40.6

[a] Reaction conditions: 70 °C, 10 mL cyclohexane, 0.05 g additive, 0.12 g catalyst, 0.08 g TBHP.
[b] All catalysts supported on graphite.

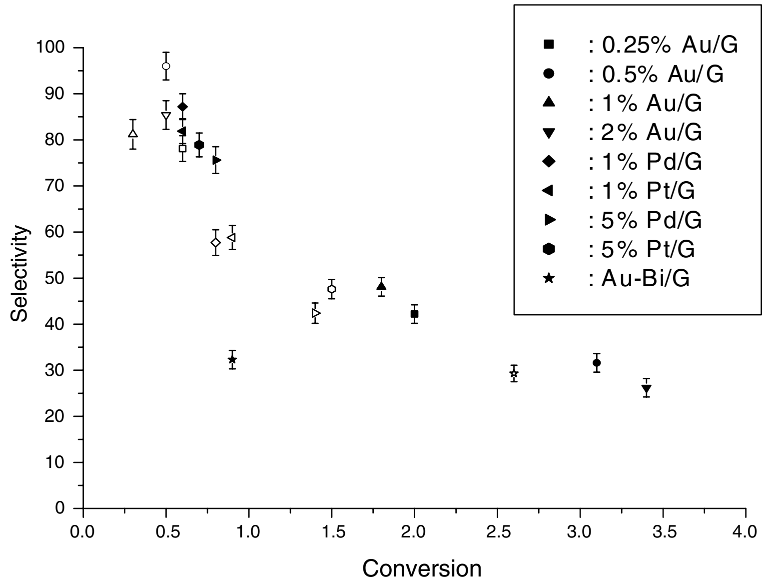

Figure 2. Relationship between cyclohexane conversion and the total selectivity to cyclohexanol and cyclohexanone, data collected at 9 h reaction time. Solid symbols represent the reaction without inhibitor 1,4-difluorobenzene. Open symbols represent the reaction with inhibitor 1,4-difluorobenzene present.

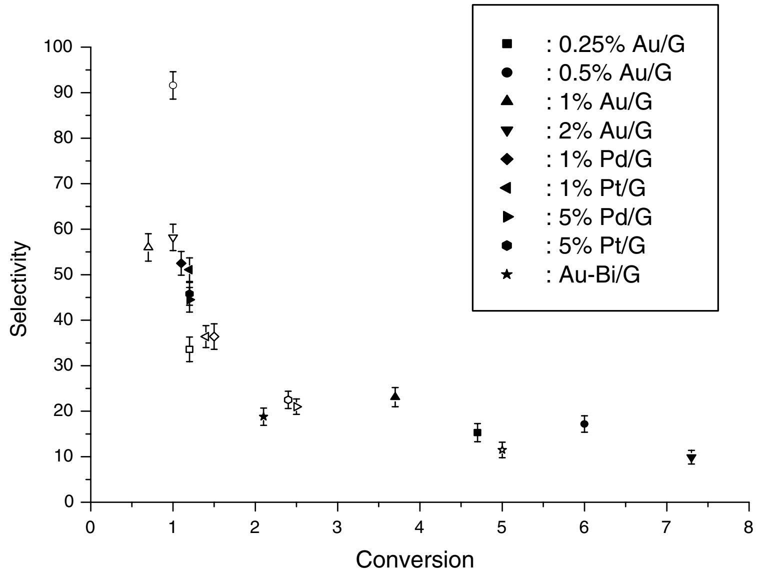

Figure 3. Relationship between cyclohexane conversion and the total selectivity to cyclohexanol and cyclohexanone, data collected at 17 h reaction time. Solid symbols represent the reaction without inhibitor 1,4-difluorobenzene. Open symbols represent the reaction with inhibitor 1,4-difluorobenzene present.

plotted on figures 2 and 3, it is apparent that they fall on the same selectivity conversion relationship. Extremely high selectivity can only be obtained in a short of time and the reaction with longer time will lead to the much loss of selectivity. Consequently, under these reaction conditions these additives do not improve catalyst performance in essence.

In a final set of experiments we investigated the effect of the addition of Bi to the gold catalyst (table 3). Bismuth is known to be a promoter in selective oxidations catalysed by Pt and Pd [25,26]. However, with the 1%Au/graphite catalyst the addition of Bi led to more active but less selective catalysts, even in the presence of 1,4-difluorobenzene which gave lower conversions in the undoped catalysts. When these data are plotted on figure 3, it is clear that they also follow the same selectivity/conversion relationship.

In summary, we have demonstrated that supported gold catalyst can be active and selective in the oxidation of cyclohexane to cyclohexanol and cyclohexanone when operated under exceptionally mild conditions of temperature and pressure. However, the gold catalyst do not exhibit significantly different behaviour from supported Pt or Pd catalysts, and the selectivity is solely a

Table 3
Cyclohexane oxidation without solvent using Bi modified Au/graphite catalysts

Catalyst	Temp (°C)	Additive	Conver (%)	Selectivity (%)		
				Cyclohexanol	Cyclohexanone	Total
Au-Bi	70	1,4-difluorobenzene	5.0	7.2	4.3	11.5
Au-Bi	70	–	2.1	12.5	6.3	18.8
Au-Bi	60	1,4-difluorobenzene	1.2	11.1	7.4	18.5
Au-Bi	60	–	1.8	9.7	6.4	16.1
Au-Bi	50	1,4-difluorobenzene	0.9	8.3	6.1	14.4
Au-Bi	50	–	1.1	6.1	4.5	10.6
Au	70	1,4-difluorobenzene	1.0	48.1	43.5	91.6
Au	70	–	6.0	11.0	6.2	17.2

[a] Reaction conditions: 70 °C, 10 mL cyclohexane, 0.05 g additives, 0.12 g catalyst, 0.08 g TBHP, 17 h; catalyst Au-Bi: 0.5% Au/graphite modified with Bi, Au: non-modified 0.5% Au/graphite.

function of conversion which in turn is a function of reaction time. It is clear that at very low conversions very high selectivities can be observed, but high selectivity under these conditions cannot be maintained at higher conversions.

Acknowledgments

This work was sponsored by Johnson Matthey and the EPSRC as part of the ATHENA and Green Oxidation projects.

References

[1] G.C. Bond and D.T. Thompson, Catal. Rev. – Sci. Eng. 41 (1999) 319.

[2] G.J. Hutchings, J. Catal. 96 (1985) 292.

[3] M. Haruta, T. Kobayashi, H. Sano and N. Yamada, Chem. Lett. 4 (1987) 405.

[4] L. Prati and M. Rossi, J. Catat. 176 (1998) 552.

[5] F. Porta, L. Prati, M. Rossi, S. Colluccia and G. Martra, Catal. Today 61 (2000) 165.

[6] C. Bianchi, F. Porta, L. Prati and M. Rossi, Top. Catal. 13 (2000) 231.

[7] S. Carretin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely and G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1329.

[8] S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G.J. Hutchings, Chem. Commun. (2002) 696.

[9] P. Landon, P.J. Collier, A.J. Papworth, C.J. Kiely and G. J.Hutchings, Chem. Commun. (2002) 2058.

[10] P. Landon, P.J. Collier, A.F. Carley, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely and G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1917.

[11] J.M. Thomas, R. Raja, G. Sankar and R.G. Bell, Acc. Chem. Res. 34 (2001) 191 and references therein.

[12] J.A. Labinger and J.E. Bercaw, Nature 417 (2002) 507.

[13] M. Dugal, G. Sankar, R. Raja and J.M. Thomas, Angew. Chem. Int. Ed. 39 (2000) 2310.

[14] J.M. Thomas, R. Raja, G. Sankar and R.G. Bell, Nature 398 (1999) 227.

[15] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinace and E.L. Pires, Appl. Catal. A211 (2001) 1.

[16] U. R. Pillai and E. Sahle-Demessie, Chem. Commun. (2002) 2142.

[17] A. Sakthivel and P. Selvam, J. Catal. 211 (2002) 134.

[18] C.L. Hill and I.A. Weinstock, Nature 388 (1997) 332.

[19] S.A. Chavan, D. Srinivas and P. Ratnasamy, J. Catal. 212 (2002) 39.

[20] M. Nowotny, L.N. Pederson, U. Hanefeld and T. Maschmeyer, Chem. Eur. J. 8 (2002) 3724.

[21] R. Raja, G. Sankar and J.M. Thomas, J. Am. Chem. Soc. 121 (1999) 11926.

[22] R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang and J. Suo, Chem. Commun. (2004) 904.

[23] G. Lü, R. Zhao, Guang Qian, Y. Qi, X. Wang and J. Suo, Catal. Lett. 97 (2004) 115.

[24] S. Golunski, R. Rajaram, N. Hodge, G.J. Hutchings and C.J. Kiely, Catal. Today 72 (2002) 107.

[25] J. Clavilier, J.M. Feliu and A. Aldaz, J. Electroanal. Chem. Interfacial Electrochem. 243 (1988) 419.

[26] P. Fordham, M. Besson and P. Gallezot, Stud. Surf. Sci. Catal. 108 (1997) 429.