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Oxidation of glycerol using supported Pt, Pd and Au catalysts

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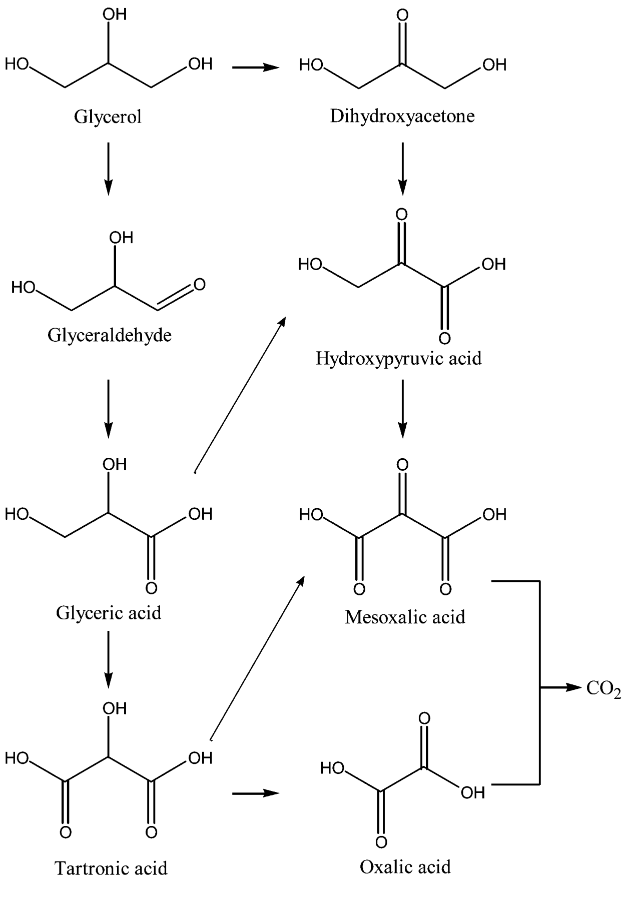
The oxidation of aqueous solutions of glycerol is described and discussed for Pd, Pt and Au nanoparticles supported on graphite and activated carbon. The oxidation in a batch reactor at 60 °C and 1 bar pressure using air as oxidant was initially investigated. Under these conditions, supported Pd and Pt catalysts give some selectivity to glyceric acid, but the main reaction products are considered to be non-desired C_1 by-products, *e.g.* CO_2, HCHO and HCOOH. In addition, under these conditions, supported Au catalysts were totally inactive. Using an autoclave with pure oxygen at 3 bar pressure gave a significant improvement in reactivity and, for Pt and Au catalysts, the formation of C_1 by-products was eliminated when NaOH was added. In particular, it was noted that, in the absence of NaOH, the Au/C catalyst was inactive. For 1 wt.% Au/graphite or activated carbon, 100% selectivity to glyceric acid at high conversion was readily achieved. The role of the base is discussed and it is proposed that the base aids the initial dehydrogenation *via* H-abstraction of one of the primary OH groups of glycerol and, in this way, the rate limiting step in the oxidation process is overcome.

Introduction

Oxidation reactions are important for the synthesis of fine chemicals. However, at present many oxidations that are carried out commercially involve stoichiometric oxidants, *e.g.* permanganate or chromic acid, and these entail the formation of significant quantities of non-desired by-products. There is, therefore, immense scope for the replacement of stoichiometric oxidants with catalytic processes using dioxygen, and the environmental benefits for this have been outlined by Sheldon and Dakka.[1] In recent years, this has spurred the investigation of a range of oxidation reactions using gas or liquid phase reagents to produce valuable intermediates or products for the chemicals industry.[2–13] In particular, the oxidation of alcohols and polyols to chemical intermediates represents a demanding target.[12] Supported platinum and palladium nanoparticles are generally acknowledged as effective catalysts for the oxidation of polyols, for example in carbohydrate chemistry for the oxidation of glucose to glucinic acid.[9,11] Glycerol is a highly functionalised molecule that is readily available from biosustainable sources, for example it can be obtained as a by-product of the utilisation of rape seed and sunflower crops. This makes glucose a particularly attractive starting point for the synthesis of intermediates, and a large number of products can be obtained from glycerol oxidation (Scheme 1). One of the key problems is the potential complexity of the products that can be formed and so control of the reaction selectivity by careful design of the catalyst is required. Glycerol oxidation, in aqueous solution, has been extensively studied using supported platinum and palladium catalysts by Gallezot and co-workers[14–16] and Kimura and co-workers.[17,18] In general, palladium catalysts were found to be more selective than platinum and high selectivities to either dihydroxyacetone[18] or glyceraldehyde[14] could be obtained by controlling the



Scheme 1

reaction conditions and, in particular, the pH of the solution. However, it has been noted that formic acid, probably resulting from the formation of oxalic acid, was also formed. It is worth noting that, in all these previous studies, mixtures of most of the potential products were formed.

In recent years, there has been immense interest in the use of gold catalysts for oxidation reactions.[19] Prati and co-workers[20–23] have shown that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols. Most recently, in our earlier communication,[24] we have shown that supported gold catalysts can be effective for glycerol oxidation and, in particular, glycerol can be oxidised to glyceric acid with 100% selectivity to glyceric acid. In this paper, we extend this earlier study and compare and contrast non-promoted supported palladium, platinum and gold catalysts for the selective oxidation of glycerol.

Experimental

Catalyst preparation

5 wt.% platinum catalysts supported on activated carbon and graphite were prepared as follows. An aqueous solution of a platinum 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.

5 wt.% palladium catalysts supported on activated carbon and graphite were prepared using method Pd-A. An aqueous solution of a palladium chloride salt (5% Pd metal by weight of support) was added to a stirred carbon slurry and reduced with formaldehyde. The slurry was allowed to settle, filtered and washed free of chloride. The catalyst was dried at 105 °C for 16 h.

A sample of 5 wt.% Pd supported on activated carbon was also prepared by the alternative method Pd-B according to Garcia *et al.*[14] A solution of $PdCl_2 \cdot 2HCl$ (23.68% Pd, Johnson Matthey, 21.11 g) in demineralised water (100 ml) was added to activated carbon (99.7 g, Johnson Matthey) and the suspension was stirred for 5 h at 25 °C. After cooling to 0 °C, the slurry was reduced with formaldehyde and, after stirring for 15 min, three successive additions of aqueous KOH (15 ml, 30%) were made and the slurry was stirred at 25 °C for a further 16 h. The catalyst was recovered by filtration and washed with water until the washings were pH neutral. The catalyst was dried at 105 °C for 16 h.

1 wt.% gold catalysts supported on activated carbon and graphite were prepared as follows. The carbon support (graphite or activated carbon, 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/C and 0.5 wt.% Au/C catalyst samples using smaller amounts of chloroauric acid.

Catalyst testing and characterisation

Glass reactor studies. Experiments at 1 bar pressure were carried out using two glass reactors (300 and 50 ml volume) equipped with an overhead stirrer (*ca.* 500 rpm). Air was passed into the reactor at a controlled flow rate *via* a calibrated mass flow controller, through a glass frit inserted into the stirred reactants. The pH of the reactants was maintained constant by the addition of aqueous NaOH (30 wt.%) using a Denver Instruments Titrator 290. In a typical experiment, the catalyst (glycerol/metal mol ratio = 500) was suspended in water (10 ml) and the slurry was heated to the required temperature with stirring. Glycerol (4.605 g, 99%, Lancaster; in 40 ml water) was then added to obtain a final glycerol solution ($1 \text{ mol } l^{-1}$ glycerol). After 10 min, air was passed through the reactants at a controlled flow rate. Samples were removed from the reaction mixture at regular intervals for analysis.

Autoclave reactor studies. These reactions were carried out using a 50 ml Parr autoclave. The catalyst was suspended in an aqueous solution of glycerol ($0.6 \text{ mol } l^{-1}$, 20 ml). The autoclave was pressurised to the required pressure with oxygen and heated to 60 °C. The reaction mixture was stirred (1500 rpm) for 3 h, following which the reaction mixture was analysed.

Product analysis. Analysis was carried out using HPLC with ultraviolet and reflective index detectors. Reactant and products were separated on an ion exclusion column (Alltech QA-1000) heated at 70 °C. The eluent was a solution of H_2SO_4 ($4 \times 10^{-4} \text{ mol } l^{-1}$). Reaction mixture samples (10 µl) were diluted with a solution of an internal standard (100 µl, $0.2 \text{ mol } l^{-1}$ isobutanol) and 20 µl of this solution was analysed. It is essential that a standard is added so that the carbon mass balance can be determined. Attempts to find a suitable internal standard that could be added prior to reaction were found to be unsuccessful as they were readily oxidised under the reaction conditions. Hence, it was found necessary to add the standard immediately following the reaction as described.

Catalyst characterisation. Samples were structurally characterised in a JEOL 2000 EX high resolution electron microscope operating at 200 kV. The catalyst powders were made suitable for TEM examination by grinding them in high purity ethanol using an agate pestle and mortar. A drop of the suspension was then deposited onto, and allowed to evaporate, on a holey carbon grid.

Results and discussion

Oxidation of glycerol using the glass reactor at 1 bar

Gallezot and co-workers[14–16] have reported that Pd/C catalysts can oxidise glycerol to glyceric acid with high selectivity at 1 bar and, hence, glycerol oxidation was investigated using the 5 wt.% Pd/C catalysts at 60 °C with air at 1 bar using the glass slurry reactor. The results are shown in Table 1. At a low air flow rate (1 ml min^{-1}) no reaction was observed with 5 wt.% Pd/carbon prepared by method Pd-A for the standard reaction conditions (glycerol/Pd mol ratio = 500). Increasing the catalyst mass did, however, result in low levels of glycerol conversion, but the mass balance to C_3 and C_2 products was extremely low (*ca.* 7%). At higher air flow rates with the 5 wt.% Pd/carbon catalyst, the conversion of glycerol increased, as did the mass balance. However, the carbon mass balance for C_3 and C_2 products remained low (<40%). Interestingly, the normalised C_3 and C_2 product selectivities, *i.e.* the selectivity calculated assuming these are the only reaction products, give very high selectivities to glyceric acid (> 70%) and these are very similar to the selectivities reported in the literature[14–16] for non-promoted catalysts. Similar results were obtained for the 5 wt.% Pd/graphite catalyst prepared by method Pd-A. In view of these results, a catalyst was prepared by method Pd-B according to the procedure of Garcia *et al.*[14] and the results are also shown in Table 1. Again, at low air flow rates, no reaction is observed. Increasing the air flow rate leads to increased glycerol conversion, and the normalised selectivity to glyceric acid is similar to that observed for the catalyst

Table 1 Oxidation of glycerol using 5 wt.% Pd/C catalysts[a]

Catalyst	Catalyst mass/g	Air[b] / ml min^{-1}	Glycerol conversion (%)	Product selectivity[c] (%) Glyceric acid	Glyceraldehyde	Tartronic acid	Oxalic acid	Mass balance[d] (%)
Pd/carbon[e]	0.320	1	0	–	–	–	–	–
Pd/carbon[e]	0.320	10	17.9	6.6 (85.7)	–	–	1.1 (14.3)	7.5
Pd/carbon[e]	0.320	30	48.3	32.3 (93.1)	–	–	2.4 (6.9)	34.7
Pd/carbon[e]	0.320	100	57.0	18.0 (76.3)	1.2 (5.1)	–	3.2 (18.6)	22.4
Pd/carbon[e]	1.230	1	9.0	2.8 (38.9)	2.4 (33.3)	–	1.9 (27.8)	7.1
Pd/carbon[e]	2.430	1	19.0	3.5 (46.6)	2.0 (26.7)	–	2.0 (26.7)	7.5
Pd/carbon[f]	0.320	1	0	–	–	–	–	–
Pd/carbon[f]	0.320	30	22.5	39.0 (94.2)	1.3 (3.1)	1.1 (2.7)	–	41.4
Pd/carbon[f]	0.320	100	73.5	62.0 (75.6)	2.0 (4.9)	16.0 (19.5)	–	80.0
Pd/graphite[g]	0.320	100	54.0[h]	4.0 (67)	1 (16.5)	–	1 (16.5)	–

[a] Reaction conditions: 60 °C, 1 bar, 21 h, pH 11, aqueous glycerol (50 ml, 1 mol l^{-1}). [b] Air flow rate through reaction. [c] Product selectivity on basis of using internal standard. Figures in parenthesis are normalised for the observed C_2 and C_3 products. [d] Determined on the basis of observed C_2 and C_3 products. [e] 5 wt.% Pd/activated carbon prepared by method Pd-A. [f] 5 wt.% Pd/activated carbon prepared according to the method of Garcia *et al.*[14] [g] 5 wt.% Pd/graphite prepared using same procedure as (e). [h] Conversion after 8 h reaction.

prepared by method Pd-A. At the highest air flow rate investigated (100 ml), the C_3 and C_2 carbon mass balance was 80% and the normalised product selectivities were similar to those reported by Garcia *et al.*[14]. However, all these studies show that there is appreciable formation of compounds other than the expected C_3 and C_2 products. This will be discussed subsequently.

There are significant differences that can be noted in the catalytic performance of the 5 wt.% Pd/carbon catalysts prepared by methods Pd-A and Pd-B. First, for the Pd-A derived catalyst, the major products comprise glyceric acid with glyceraldehyde and oxalic acid whereas, for the Pd-B derived catalyst, the products comprise glyceric acid with glyceraldehyde and tartronic acid. It is possible that tartronic acid is oxidised to oxalic acid, and the difference in activity of the two catalysts may account for this. However, more importantly, the two catalysts show different conversion with time-on-line profiles for glycerol oxidation (Fig. 1). The catalyst prepared by method Pd-A exhibits the expected dependence of conversion with reaction time. The catalyst prepared by method Pd-B, however, shows a marked induction period, during which no glycerol conversion is observed. This behaviour was noted for all the reaction conditions for which this catalyst was investigated. There are two potential reasons for this observation. First, the catalyst surface is initially incompletely reduced or is covered by an inhibitor or poison (*e.g.* chloride or high molecular weight products originating from reactions of the initial reducing agent, formaldehyde) or, secondly, the catalyst leaches Pd into solution and this subsequently acts on an active homogeneous oxidation catalyst. Following the reactions, the solution was analysed and no Pd was found to have been leached, hence the first explanation appears to be preferred. Following catalyst preparation, the catalyst was reduced at room temperature and it is possible that the catalyst reduction was not complete under such conditions. Glycerol can act as a reducing agent and, during the initial reaction period, the reduction process could be completed leading to the observation of an induction period. However, it is unlikely that glycerol is a stronger reducing agent towards Pd^{2+} compared with formaldehyde, hence it is more likely that the initial induction period noted with this preparation is related to the removal of inhibitors.

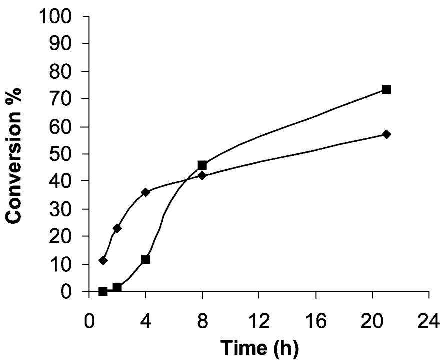


Fig. 1 Effect of reaction time on glycerol conversion using 5 wt.% Pd/C catalysts. Key : ◆ Pd/C prepared method Pd-A, ■ Pd/C prepared using method Pd-B of Garcia *et al.*[14] Reaction conditions : 60 °C, 1 bar, pH 11.

The 5 wt.% Pd/carbon catalysts derived by method Pd-A and Pd-B (Garcia *et al.* method) were compared by transmission electron microscopy and typical micrographs are presented in Fig. 2. The Pd-A derived catalyst, shown in Fig. 2(a) and at higher resolution in Fig. 2(b), comprises a very fine dispersion of metallic Pd particles which exhibit a distinct bimodal size distribution. The majority of Pd particles were in the 2–5 nm site range (mean 4 nm), whereas larger particles in the 8–12 nm size range were also occasionally present. The Pd-B derived catalyst (Fig. 2(c)) also exhibited a bimodal size distribution of Pd, with most particles being in the 3–7 nm range (mean 5 nm) along with a significant number of larger ones in the 10–20 nm range.

The effect of *in situ* reduction with hydrogen (99%, 100 ml min^{-1}, 60 °C, 30 min) of the Pd/C catalyst prepared method Pd-A was investigated and the results are shown in Fig. 3. For the 5 wt.% Pd/graphite catalyst, the *in situ* reduction step did not affect the glycerol conversion notably (Fig. 3(a)) whereas, for the 5 wt.% Pd/carbon catalyst, the *in situ* reduction did increase the conversion significantly. In both cases, the selectivity to glyceric acid was improved (Fig. 3(b)) and, during the initial stages of the reaction, very high mass balances to C_3 and C_2 products are observed (Fig. 3(c)). It is considered that the *in situ* hydrogen reduction treatment removes traces of deleterious surface PdO species that form readily after catalyst preparation.[12]

5 wt.% Pt/carbon was investigated for glycerol oxidation under the same conditions and the results are given in Table 2 and Fig. 4. The Pt catalyst was found to be more active than the Pd catalysts and significant glycerol conversion was observed even for the lowest air flow rate. Interestingly, the only C_3 or C_2 product observed is glyceric acid, together with minute traces of glyceraldehyde, but the C_3 and C_2 carbon

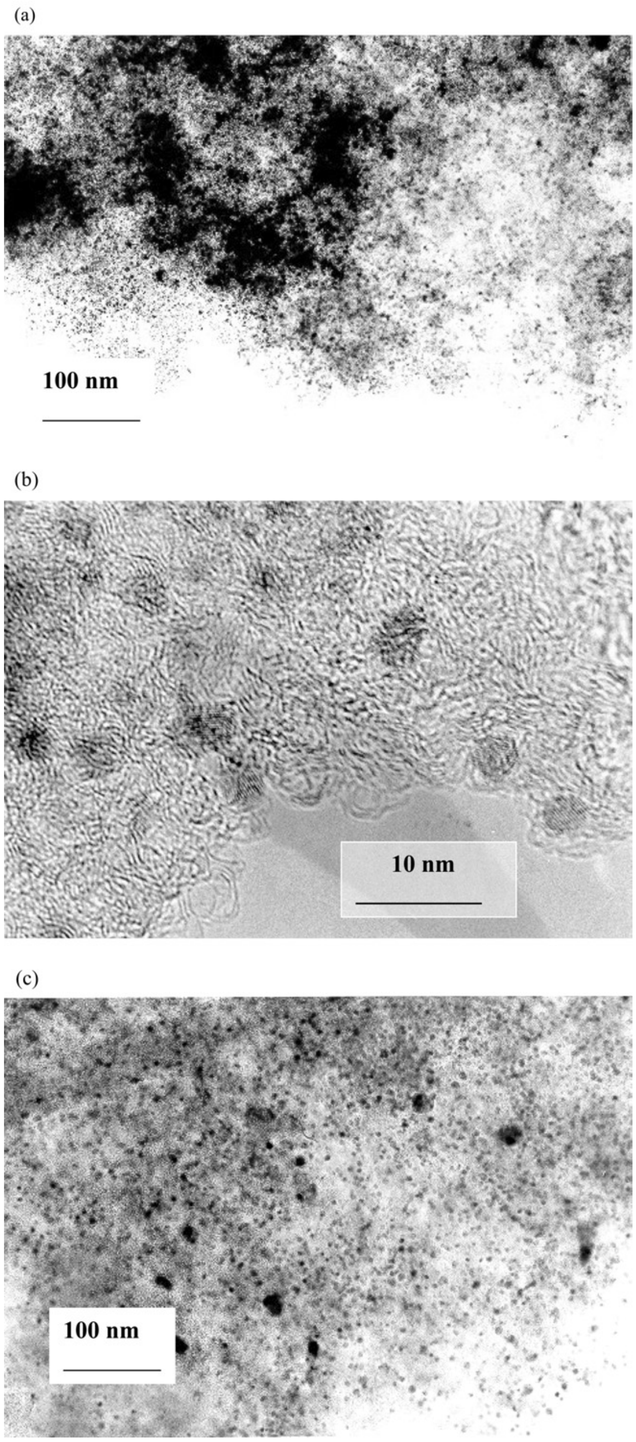


Fig. 2 (a) Bright field image and (b) high resolution lattice image of the 5 wt.% Pd/carbon catalyst derived from method Pd-A; (c) shows a bright field image of the 5 wt.% Pd/carbon catalyst derived from method Pd-B.

mass balance was very low for all conditions examined (<50%). The effect of reduction was also investigated for the Pt/carbon catalyst (Fig. 4). During the initial stages of the reaction, the use of *in situ* or *ex situ* reduction does not have a significant effect, although the eventual glycerol conversion observed with the *in situ* reduced catalyst was significantly higher. Experiments with 5 wt.% Pt/graphite for the oxidation of glycercol gave similar results.

Representative electron micrographs of the 5 wt.% Pt/carbon sample are shown in Fig. 5. This catalyst shows a highly dispersed and very uniform distribution of Pt nanoparticles over the activated carbon support. The measured particle size range was 1.5–3 nm with most particles being sub-2 nm in diameter.

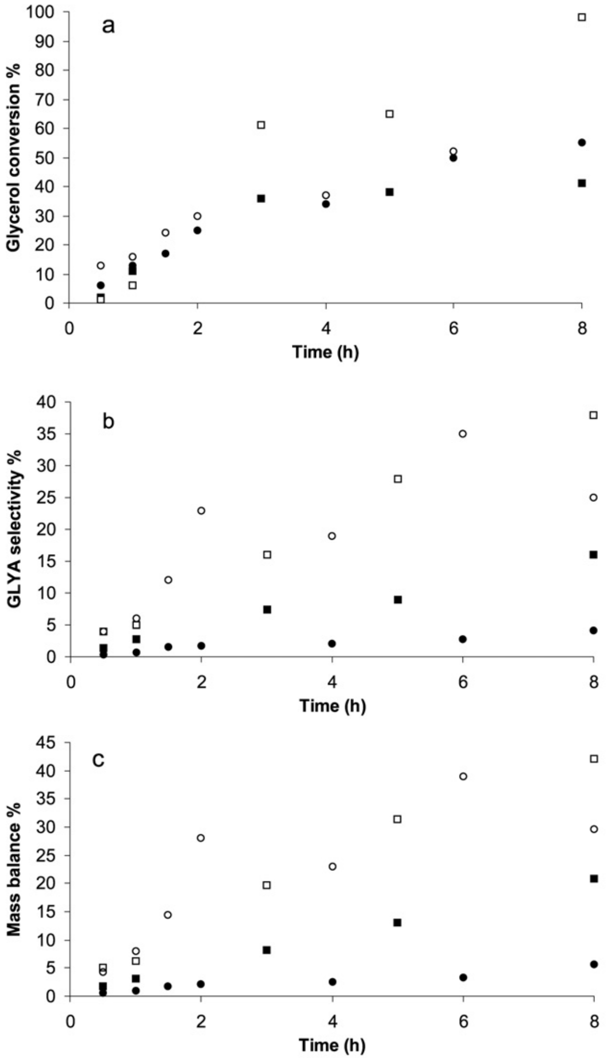


Fig. 3 Effect of *in situ* reduction on 5 wt.% Pd/C catalysts. Key : □ Pd/carbon, ○ Pd/graphite; closed symbols no *in situ* reduction; open symbols with *in situ* reduction. Reaction conditions : 60 °C, 1 bar, pH 11. (a) Conversion, (b) glyceric acid selectivity, (c) C_2 and C_3 carbon mass balance.

The low mass balance for the formation of C_2 and C_3 products using 5 wt.% Pd/C and 5 wt.% Pt/C catalysts could be due to three causes : (a) the polymerisation of reaction products to polymers not observable by the hplc analytical method, (b) the adsorption of reaction products onto the

Table 2 Glycerol oxidation over 5 wt.% Pt/C catalyst[a]

Air/ ml min^{-1}	Glycerol conversion (%)	Product selectivity[b] (%) Glyceric acid	Glyceraldehyde	Mass balance[c] (%)
1	29.6	6.7 (100)	tr	6.7
10	47.0	17.4 (100)	tr	17.4
30	60.0	47.5 (100)	0	47.5
100	89.0	41.0 (100)	tr	41.0

[a] 5 wt.% Pt/activated carbon; reaction conditions: 60 °C, 21 h, 1 bar, pH 11, 0.320 g catalyst, (50 ml, 1 mol l^{-1}). [b] Product selectivity determined on basis of analysis using internal standard Figures in parenthesis are normalised for the observed C_3 products. [c] Determined on the basis of C_2 and C_3 products observed.

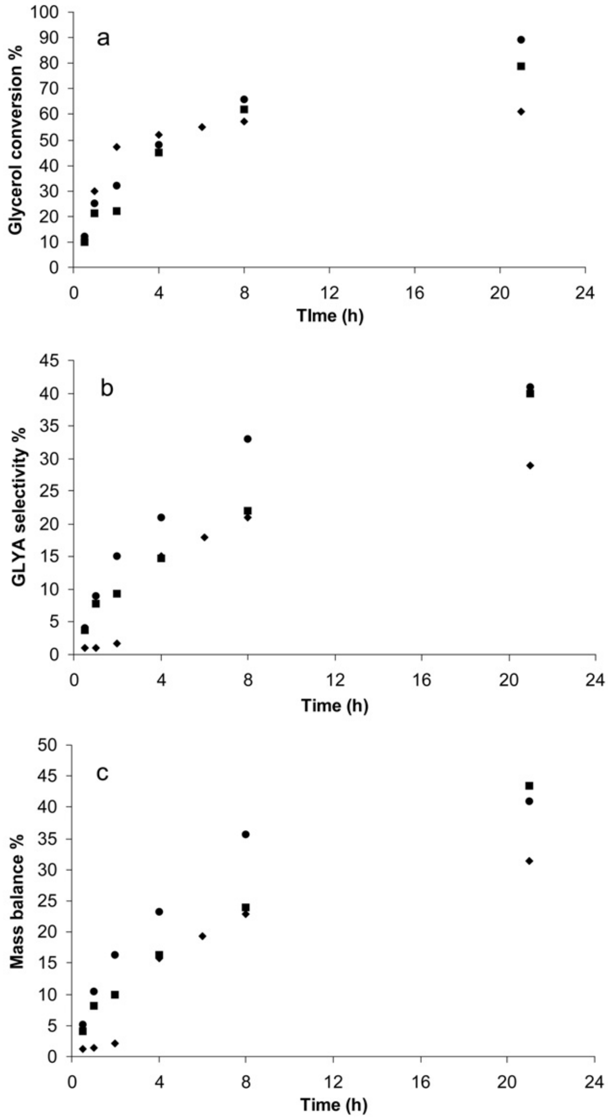


Fig. 4 Glycerol oxidation over Pt/carbon catalysts showing effect of reduction conditions. Key : ■ unreduced; ◆ reduced *ex situ*; ● reduced *in situ*. Reaction conditions, 60 °C, 1 bar, pH 11. (a) Conversion, (b) glyceric acid selectivity, (c) C_2 and C_3 carbon mass balance.

carbon supports or (c) the sequential oxidation of the C_3 and C_2 oxidation products to CO_2 and formic acid.

To examine the possible formation of polymers, reactions were carried out using mixtures of dihydroxyacetone, glyceric acid and glyceraldehyde with the 5 wt.% Pd/carbon catalyst. The reaction mixtures were analysed for polymeric products using hplc and no appreciable formation of oligomers and polymers was observed.

To determine if reaction products were being adsorbed onto the carbon support during the reaction, the catalysts were investigated after reaction using thermal gravimetric analysis (TGA). Only the desorption of water, the reaction solvent, was observed and, hence, it is concluded that the adsorption of the partial oxidation products is not occurring on the catalyst.

It was, therefore, considered that the low mass balance was most likely to be due to the sequential oxidation of the C_3 partial oxidation products. To examine this possibility, the stability of the reaction products was investigated under the standard reaction conditions, and the results are shown in Table 3. It is clear that glyceric acid and glyceraldehyde are particularly unstable under these conditions. Hydroxy pyruvic acid and oxalic acid are much more stable, and dihydroxyacetone is the most stable. These results are in agreement with a previous study of 1,3-butanediol oxidation by Lin and Sun[25] in which CO_2 was observed as a reaction product, however, this study involves the electrocatalytic oxidation in acidic medium and, consequently, operates *via* a different mechanism than that in basic medium, the present reaction conditions. The formation of CO_2 as a by-product of alcohol oxidation using Pt and Pd catalysts has been noted by Prati and Rossi.[26] In view of this, experiments were conducted to investigate the formation of CO_2, and it was confirmed that CO_2 constitutes a major factor of the carbon balance for these oxidation reactions. In addition, it is considered that carbon monoxide and formic acid may also be formed. The determination of a closed mass balance is complicated by the solubility of CO_2 and other C_1 products, *e.g.* formaldehyde and formic acid, in the reaction medium since sodium carbonate and other soluble products will be formed.

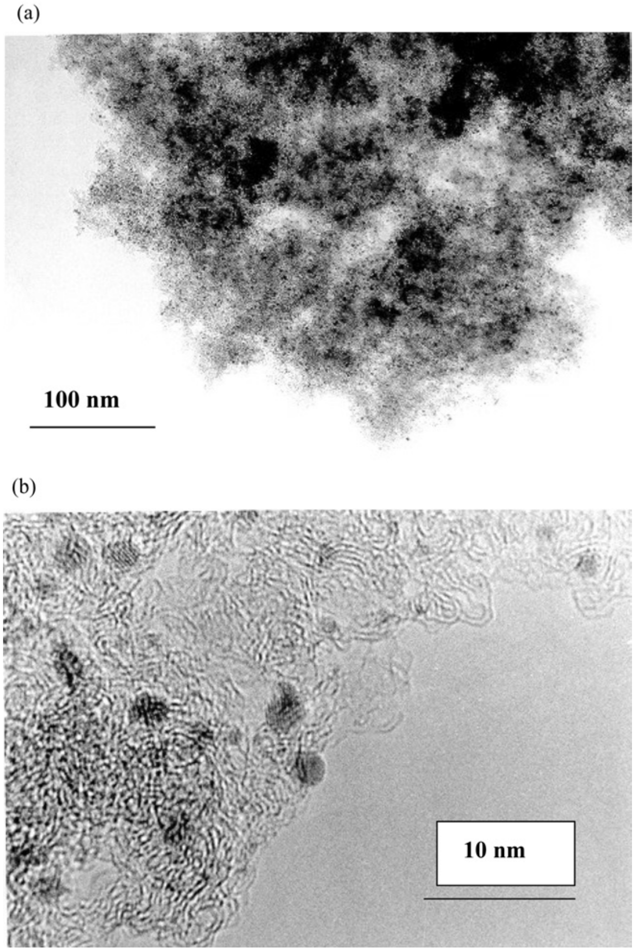


Fig. 5 (a) Bright field image and (b) high resolution lattice image of the 5 wt.% Pt/carbon catalyst.

A series of experiments were carried out using the glass slurry reaction with Au/C catalysts. No conversion was observed under the reaction conditions at the low oxygen partial pressure. It was, therefore, decided to investigate the oxidation of glycerol at a higher oxygen pressure using an autoclave reactor.

Oxidation of glycerol using an autoclave reactor

The oxidation of glycerol with dioxygen was investigated using an autoclave reactor at elevated pressure with both supported Pt and Pd catalysts, and the results are shown in Table 4. As expected under these conditions, the carbon and graphite supports were inactive. For the 5 wt.% Pt/carbon catalyst, in the

Table 3 Product stability over 5 wt.% Pt/C catalysts[a]

			Products[b] (%)			
Substrate	Reaction time/h	Conversion (%)	Hydroxy pyruvic acid	Oxalic acid	Glyceric acid	Glyceraldehyde
Dihydroxyacetone[c]	21	19.4	13.7	2.1	6.7	2.8
Glyceric acid[d]	4	100	tr	tr	–	0
Glyceraldehyde[e]	21	100	0	0	0	–
Hydroxy pyruvic acid[f]	21	100	–	91.0	0	0
Oxalic acid[g]	7	90	0	–	0	0

[a] 5 wt.% Pt/activated carbon; reaction conditions: 60 °C, pH 11, 1 bar, air 100 ml min^{-1}, water as solvent. [b] Observed products by hplc, CO_2 and HCOOH not quantified. [c] Calcium salt, 0.05 mol l^{-1}. [d] 1 mol l^{-1}. [e] 0.1 mol l^{-1}. [f] 0.2 mol l^{-1}. [g] 0.5 mol l^{-1}.

Table 4 Oxidation of glycerol using Pt/C catalysts in an autoclave reactor[a]

				Product selectivity[b] (%)				
Catalyst	NaOH/glycerol mol ratio	Glycerol/metal mol ratio	Glycerol conversion (%)	Glyceric acid	Glyceraldehyde	Oxalic acid	Tartronic acid	Mass balance[c] (%)
None	1	–	0	–	–	–	–	–
None	1	–	0	–	–	–	–	–
Carbon	1	–	0	–	–	–	–	–
Graphite	1	–	0	–	–	–	–	–
5 wt.% Pt/carbon	0	500	27.0	27.8 (32.6)	0 (0)	57.4 (17.4)	0 (0)	85.2
5 wt.% Pt/carbon	0.5	500	48.0	45.7 (85.1)	6.0 (11.2)	2.0 (3.7)	0 (0)	53.7
5 wt.% Pt/carbon	1.0	500	63.1	73.7 (75.2)	21.0 (21.4)	0 (0)	3.1 (3.2)	98.0
5 wt.% Pt/carbon	2.0	500	56.0	69.0 (69.7)	30.0 (30.3)	0 (0)	0 (0)	99.0
5 wt.% Pt/carbon	1.0	100	88.0	54.5 (70.3)	0 (0)	0 (0)	23 (29.7)	77.5
10 wt.% Pt/carbon	1.0	500	53.0	50.0 (96.6)	4.0 (7.4)	0 (0)	0 (0)	54.0
5 wt.% Pt/graphite	1.0	500	58.6	65.7 (69.7)	26.9 (28.6)	0 (0)	1.6 (1.9)	94.2
5 wt.% Pd/carbon	1.0	500	57.2	67.0 (78.3)	6.4 (7.5)	0 (0)	12.2 (14.2)	85.6
5 wt.% Pd/graphite	1.0	500	53.0	50.0 (77.1)	7.5 (11.4)	0 (0)	7.5 (11.4)	66.0

[a] Reaction conditions: 60 °C, 3 h, water (20 ml), catalyst (50 mg), p_{O_2} 3 bar, stirring speed 1500 rpm. [b] Product selectivity determined on basis of analysis using internal standard. Figures in parenthesis are normalised for the observed C_2 and C_3 products. [c] Determined on basis of observed C_2 and C_3 products.

absence of sodium hydroxide, the main product was oxalic acid formed by oxidative cleavage, although an appreciable selectivity to glyceric acid was also observed. The presence of sodium hydroxide markedly decreased the selectivity to oxalic acid. The principal products were now glyceric acid and glyceraldehyde. In particular, the C_2 and C_3 carbon mass balance was now typically 98–99% indicating that, under these conditions, the oxidative cleavage to C_1 products (*i.e.* CO_2, H_2CO, HCOOH) had essentially been eliminated. Interestingly, increasing the catalyst concentration, so that the glycerol/metal ratio was 100, instead of 500, decreased the C_2 and C_3 carbon mass balance, as did increasing the metal loading of the Pt to 10 wt.% Pt/carbon. This indicates that the catalyst metal loading and concentration require careful optimisation for this complex oxidation reaction to enable the formation of non-desired C_1 by-products to be avoided. A range of alternative bases was also investigated and the results are given in Table 5. It is apparent that the highest glycerol conversion and highest selectivity to glyceric acid is observed with NaOH. Interestingly, the use of $NaNO_3$ also leads to a high C_2 and C_3 carbon mass balance, but the selectivity is almost exclusively to oxalic acid. However, with $NaNO_3$, there is no significant effect on glycerol conversion when compared with the reaction in the absence of base. This

Table 5 Oxidation of glycerol using 5 wt.% Pt/C catalysts in the presence of different bases[a]

		Product selectivity[b] (%)				
Base	Glycerol conversion	Glyceric acid	Glyceraldehyde	Oxalic acid	Tartronic acid	Mass balance[c] (%)
None	27.0	27.8 (22.6)	0 (0)	57.4 (67.4)	0 (0)	85.2
LiOH	48.9	52.0 (74.2)	19.0 (25.8)	0 (0)	0 (0)	70.0
NaOH	63.1	73.7 (75.4)	21.0 (21.4)	0 (0)	3.1 (3.2)	97.8
$NaNO_3$	36.0	14.0 (14.6)	0 (0)	85.0 (85.4)	0 (0)	99.0
KOH	35.4	87.0 (88.8)	11.0 (11.2)	0 (0)	0 (0)	98.0
RbOH	37.0	13.7 (75.3)	4.5 (24.7)	0 (0)	0 (0)	18.2
CsOH	52.0	18.0 (100)	0 (0)	0 (0)	0 (0)	18.0

[a] 5 wt.% Pt/activated carbon; reaction conditions: 3 h, 60 °C, p_{O_2} 3 bar, water (20 ml), glycerol/metal mol ratio = 500, base/glycerol mol ratio = 1./0, catalyst (50 mg), stirring speed 1500 rpm. [b] Product selectivity determined on basis of analysis using internal standard. Figures in parenthesis are normalised on the basis of observed C_2 and C_3 products. [c] Determined on basis of observed C_2 and C_3 products.

Table 6 Oxidation of glycerol using 1 wt.% Au/C catalysts[a]

Catalyst	Glycerol/mmol	p_{O_2}/bar	Glycerol/metal mol ratio	NaOH/mmol	Glycerol conversion (%)	Selectivity (%)		
						Glyceric acid	Glyceraldehyde	Tartronic acid
1 wt.% Au/activated carbon	12	3	538[b]	12	56	100	0	0
1 wt.% Au/graphite	12	3	538[b]	12	54	100	0	0
1 wt.% Au/graphite	12	6	538[b]	12	72	86	2	12
1 wt.% Au/graphite	12	6	538[b]	24	58	97	0	3
1 wt.% Au/graphite	6	3	540[c]	12	56	93	0	7
1 wt.% Au/graphite	6	3	540[c]	6	43	80	0	20
1 wt.% Au/graphite	6	3	214[d]	6	59	63	0	12
1 wt.% Au/graphite	6	3	214[d]	12	69	82	0	18
1 wt.% Au/graphite	6	6	214[d]	6	58	67	0	33
1 wt.% Au/graphite	6	6	214[d]	12	91	92	0	6
1 wt.% Au/graphite	6	6	214[d]	0	0			

[a] 60 °C, 3 h, H_2O (and 20 ml), stirring speed 1500 rpm. [b] 220 mg catalyst. [c] 217 mg catalyst. [d] 450 mg catalyst.

indicates that the addition of OH^- is important for the activation of glycerol and this will be commented upon subsequently. The results also indicate that Na^+ prevents the subsequent oxidation of oxalic acid to carbon oxides. The other group 1 metal cations are not as effective as Na^+, although KOH did promote the formation of glyceric acid with very high selectivity (87%).

Supported Pd catalysts (Table 4) also give high selectivities to glyceric acid, but the selectivities and C_2 and C_3 carbon mass balance was much lower than with the corresponding supported Pt catalyst. Interestingly, under the same conditions, the 5 wt.% Pt and Pd catalysts supported on either activated carbon or graphite give very similar glycerol conversion.

The oxidation of glycerol with dioxygen was also investigated using 1 wt.% Au/C catalysts in an autoclave and the results are given in Table 6. NaOH was added as a base since, in the absence of NaOH, no glycerol conversion was observed. In addition, as noted earlier, the carbon supports were also inactive for glycerol oxidation under these conditions, even when NaOH was present. For all the data presented in Table 6, the carbon mass balance was 100% indicating that, under these conditions, supported Au/C catalysts are extremely selective for this reaction and no C_1 or C_2 by-products were detected. In addition, it is apparent that the selectivity to glyceric acid and the glycerol conversion are very dependent upon the glycerol/NaOH ratio. In general, with high concentrations of NaOH, exceptionally high selectivities to glyceric acid can be observed. However, decreasing the concentration of glycerol, and increasing the mass of the catalyst and the concentration of oxygen, leads to the formation of tartronic acid *via* consecutive oxidation of glyceric acid. Interestingly, this product is stable with these catalysts. It is apparent that, with careful control of the reaction conditions, 100% selectivity to glyceric acid can be obtained with 1 wt.% Au/C. For comparison, the supported Pd/C and Pt/C always gave other C_3 and C_2 products in addition to glyceric acid and, in particular, also gave some C_1 by-products. In a final set of experiments, catalysts with lower Au concentrations were investigated. For catalysts containing 0.25 or 0.5 wt.% Au supported on graphite, lower glycerol conversions were observed (18% and 26% respectively as compared to 54% for 1 wt.% Au/graphite under the same conditions) and lower selectivities to glyceric acid were also observed. The previous studies for diol oxidation by Prati and co-workers[20–23] have also shown that the conversion is dependent on the Au loading upon the support. This is possibly due to a particle size effect of the Au nanoparticles on the support. For gold as a CO oxidation catalyst, it has been shown that the activity is highly dependent on the particle size, and the optimum size is *ca.* 2–4 nm.[19] In view of this, the Pd, Pt and Au supported catalysts were characterised using TEM. Representative electron micrographs of the 1 wt.% Au/graphite and 1 wt.% Au/carbon materials are shown in Figs. 6(a) and 6(b) respectively. In the 1 wt.% Au/graphite specimen, Au particles as small as 5 nm and as large as 50 nm in diameter were detected. The majority, however, were about 25 nm in size and were multiply twinned in character. Decreasing the loading to 0.5 wt.% or 0.25 wt.% did not appreciably change the particle size distribution; the particle number density per unit area was observed to decrease proportionately however, which may be correlated to the decrease in glycerol

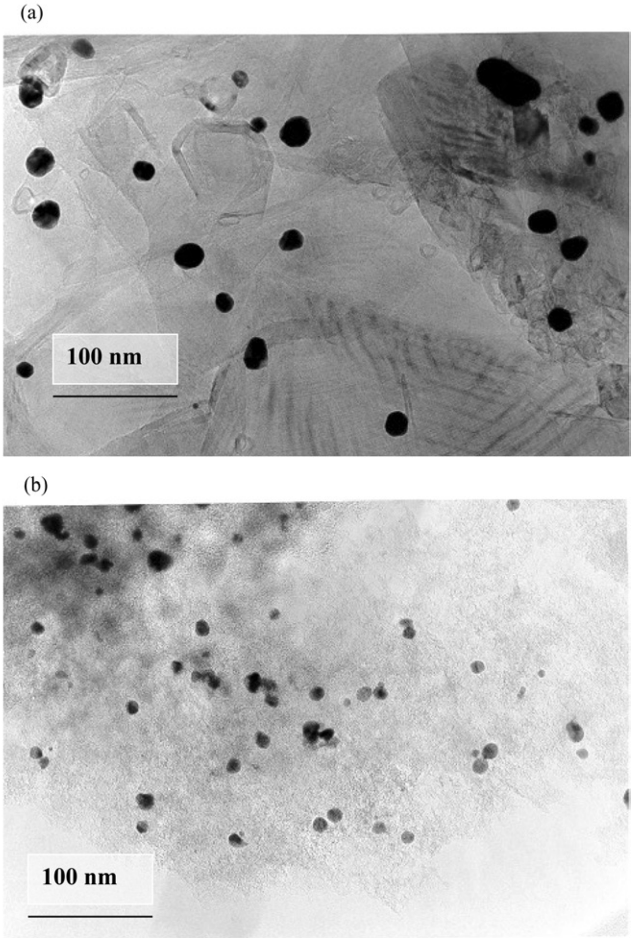


Fig. 6 Bright field transmission electron micrographs of (a) 1 wt.% Au/graphite and (b) 1 wt.% Au/carbon.

conversion and selectivity to glyceric acid. The 1 wt.% Au/carbon specimen (Fig. 6(b)) showed a considerably narrower particle size distribution (15–30 nm) with the 15 nm size range being predominant. It is interesting to note that, for both types of carbon supports, the Au particles were considerably larger than the 2–4 nm size that is considered to be optimal for low temperature CO oxidation, yet they were still highly active for the glycerol to glyceric acid reaction.

The role of OH^- requires further comment. It is noted that, for supported Pd and Pt catalysts, the addition of OH^-, as NaOH, increases the conversion of glycerol. However, for Au/C catalysts, the presence of OH^- is essential to observe any glycerol oxidation. It is proposed that, in the absence of a base, the initial dehydrogenation of glycerol, *via* H-abstraction, which must be the first step in the oxidation process, is not possible for the Au/C catalyst and is slow for the Pd/C and Pt/C catalysts. In the presence of base, the H^+ is readily abstracted from one of the primary hydroxyl groups of glycerol for form glycerate, thereby overcoming the rate limiting step of the alternative oxidation pathway. Hence, it is proposed that the oxidation mechanism of glycerol with Au catalysts in the presence of base proceeds *via* an initial deprotonation pathway as has been previously observed.[26–28]

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References

1 R. A. Sheldon and J. Dakka, *Catal. Today*, 1994, **19**, 215.
2 K. Heyns and H. Paulsen, *Angew. Chem.*, 1957, **69**, 600.
3 H. E. J. Hendriks, B. F. M. Kuster and G. B. Marin, *Carbohydr. Res.*, 1990, **204**, 121.
4 T. Mallat and A. Baiker, *Catal. Today*, 1994, **19**, 247.
5 F. R. Venema, J. A. Peters and H. van Bekkum, *J. Mol. Catal.*, 1992, **77**, 75.
6 A. Abbadi and H. van Bekkum, *Appl. Catal. A*, 1995, **124**, 407.
7 A. Abbadi and H. van Bekkum, *J. Mol. Catal. A*, 1995, **97**, 111.
8 P. Gallezot, S. Tretjak, Y. Christidis, G. Mattioda and A. Schouteeten, *J. Catal.*, 1993, **142**, 729.
9 M. Besson, P. Gallezot, F. Lahmer, G. Flèche and P. Fuertes, *J. Catal.*, 1995, **152**, 116.
10 P. Fordham, M. Besson and P. Gallezot, *Appl. Catal. A*, 1995, **133**, L179.
11 J. C. Beziat, M. Besson and P. Gallezot, *Appl. Catal. A*, 1996, **135**, L7.
12 M. Besson and P. Gallezot, *Catal. Today*, 2000, **57**, 127.
13 P. C. C. Smits, B. F. M. Kuster, K. van der Wiele and H. S. van der Baan, *Appl. Catal.*, 1987, **33**, 83.
14 R. Garcia, M. Besson and P. Gallezot, *Appl. Catal. A*, 1995, **127**, 165.
15 P. Fordham, R. Garcia, M. Besson and P. Gallezot, *Stud. Surf. Sci. Catal.*, 1996, **101**, 161.
16 P. Gallezot, *Catal. Today*, 1997, **37**, 405.
17 H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi and Y. Inaga, *Appl. Catal. A*, 1993, **96**, 217.
18 H. Kimura, *Appl. Catal. A*, 1993, **105**, 143.
19 G. C. Bond and D. Thompson, *Cat. Rev.-Sci. Eng.*, 1999, **41**, 319.
20 L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552.
21 F. Porta, L. Prati, M. Rossi, S. Colluccia and G. Martra, *Catal. Today*, 2000, **61**, 165.
22 C. Bianchi, F. Porta, L. Prati and M. Rossi, *Top. Catal.*, 2000, **13**, 231.
23 L. Prati, *Gold Bull.*, 1999, **32**, 96.
24 S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G. J. Hutchings, *Chem. Commun.*, 2002, 696.
25 N. H. Lin and S. G. Sun, *J. Electroanal. Chem.*, 1998, **448**, 5.
26 L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552.
27 K. G. Griffin, P. Johnston, S. Bennett and S. Kaliq, *Abstracts 4th World Congress Oxidation Catalysts*, Berlin/Potsdam, September 2001, Dechema, Frankfurt, 2001, vol. 1, p. 423.
28 T. Mallat and A. Baiker, *Catal. Today*, 1994, **19**, 1247.