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## Factors affecting activity and selectivity in the oxidation of glycerol promoted by platinum catalysts

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The kinetics of the catalytic oxidation of glycerol in water solutions by  $O_2$  gas, promoted by silica-supported platinum catalysts, was characterized. The reaction was optimized as a function of temperature, glycerol concentration, and oxygen flow rates. Critically, it was observed that, at least in batch reactors, both activity and primary selectivity (between the terminal and central alcohol groups, to yield glyceraldehyde and dihydroxyacetone, respectively) depend strongly on the extent of conversion of the reaction, a result that may call into question some of the conclusions reached for this system in previous studies. It was determined that the observed changes are mainly due to a reversible poisoning of the catalyst by dihydroxyacetone (and possibly other primary products), not to a secondary effect from subsequent conversion of glyceraldehyde to glyceric acid or other products. In addition, it was found that the conversion of a fresh reaction mixture with a recycled catalyst after mild reconditioning, or even after no treatment at all, displays almost the same activity and selectivity as in the initial catalytic run. Multiple use of the catalyst does lead to slow deactivation, presumably because of a buildup of carbonaceous deposits on the surface, and more stringent pretreatments cause irreversible Pt nanoparticle sintering.

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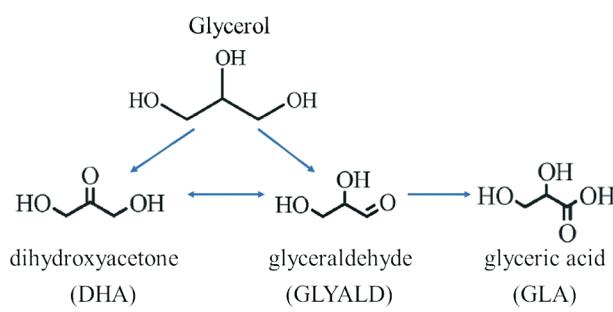
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## 1 Introduction

Glycerol, being a small but complex molecule with several functionalities, is a potentially useful feedstock for the production of fine chemicals. Specifically, the selective mild oxidation of glycerol (GLY) may yield dihydroxyacetone (DHA), glyceraldehyde (GLYALD), and/or glyceric acid (GLA) (Fig. 1); DHA is the main active ingredient in sunless tanning skin care preparations and other cosmetics, and GLA is widely used in medicine because of its role as a metabolite in the glycolysis cycle and also as an intermediate in the synthesis of amino acids and other fine chemicals.<sup>1–5</sup> The use of glycerol as a starting material in the chemical industry has, to date, not been commercially viable, but the recent interest in biofuel conversion, in which glycerol is a by-product, has made this idea more appealing. There is a need to develop selective processes to produce individual products from the conversion of glycerol.

Catalysts made out of late transition metals have shown some promise for this application. However, the published research in this area is sometimes confusing and not conclusive in terms of how to select the best catalysts for each individual application. In terms of the selective oxidation of glycerol, the subject of this report, early work used somewhat

stringent conditions and often led to the production of multiple highly oxidized products.<sup>6–8</sup> It has been repeatedly shown that selectivity toward the oxidation of the secondary alcohol group can be enhanced by the addition of Bi to Pt catalysts,<sup>6,8–17</sup> but the catalytic performance also varies significantly when using acidic *versus* basic media,<sup>3,7,11,18</sup> and only limited research has been carried out under neutral



**Fig. 1** Reaction scheme for the early steps of the partial oxidation of glycerol (GLY). The diagram highlights the reactions that define the primary selectivity in terms of oxidation of the primary alcohol group *versus* the secondary alcohol group, to yield glyceraldehyde (GLYALD) *versus* dihydroxyacetone (DHA), as well as the sequential nature of the steps that produce glyceric acid (GLA), the product of oxidation of GLYALD. The potential interchange between DHA and GLALD is also indicated, although that step was not observed in this study; it is a reaction that has been invoked to explain past data obtained under basic conditions.<sup>4</sup>



conditions. The most tested metals for this catalysis have been Pt and Pd,<sup>19,20</sup> although more recent studies with gold have shown some promising results in terms of selectivity; these typically favor oxidation of the primary OH moieties to GLA<sup>13,21,22</sup> and are inactive in the presence of bases.<sup>23,24</sup>

Many other parameters related to the characteristics of the catalyst as well as the operating conditions have been shown to influence the activity and selectivity of glycerol oxidation, including the nature of the support,<sup>20,25,26</sup> which often is a form of activated carbon,<sup>6,10,19,27</sup> the catalyst preparation method,<sup>16,18</sup> the metal loading, particle size, and particle shape,<sup>13,17,22,28,29</sup> the type of reactor used,<sup>9</sup> and the reaction conditions, including temperature and oxygen pressure.<sup>16</sup> Unfortunately, many of the published studies of this system have involved a limited number of samples and experiments as well as varying reaction conditions, a fact that makes it difficult to compare results across the different sets of data. Only a few investigations have reported systematic kinetic studies as a function of specific reaction parameters.

Here we set to redress these shortcomings by investigating the performance of simple Pt/SiO<sub>2</sub> catalysts for the oxidation of glycerol in water as a function of some of the critical parameters mentioned above. Our focus has been on the characterization of the selectivity of the partial oxidation of glycerol with molecular oxygen, with particular emphasis on the primary branching ratio between oxidation at the primary alcohol moiety and that at the secondary alcohol moiety (to yield GLYALD and DHA, respectively, see Fig. 1) as well as on the relative rates of the primary oxidation of the primary alcohol to GLYALD *versus* its sequential conversion to GLA (Fig. 1). We find that total activity and selectivity toward DHA and GLA both increase with temperature. The reaction yields increase proportionally with the concentration of GLY in the water solution, but that is accompanied by a slight loss of selectivity toward the oxidation to GLYALD. Increases in the flow of oxygen lead to slight decreases in activity, presumably because of partial oxidation of the metal. Different reduction pre-treatments with H<sub>2</sub> and O<sub>2</sub> were tested, and the degree of recyclability of the catalyst was explored as well. Finally, the catalytic performance was characterized as a function of metal loading. Perhaps the most interesting result from our work, and what we believe to be the most important contribution from this study, is that the reaction primary selectivity changes significantly as the reaction progresses (in a batch reactor). Those changes are seen in the early stages of the reaction and are not due to further conversion of the primary products to other secondary molecules but rather to reversible poisoning by the DHA that builds up in the reaction mixture over time.

## 2 Experimental details

The Pt/SiO<sub>2</sub> catalysts were synthesized by aqueous impregnation of silica supports with H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. The precursor and support were dissolved separately in water and stirred for 30 min, and the two mixtures were combined and stirred further

overnight at room temperature. The water was removed by using a rotavapor set at 345 K until the solid was completely dry, after which it was crushed into a powder. All catalysts were calcined at 675 K under air for 4 hours and then reduced at 625 K under H<sub>2</sub> flow for 3 hours before reaction. Transmission electron microscopy (TEM) characterization of the catalysts was carried out by using a PHILIPS TECNAI 12 instrument (120 kV accelerating voltage), using Formvar/Carbon Film 400 mesh grids. Four catalysts were prepared in this work, with metal loadings of 0.2, 1.0, 5.0, and 10 wt%, which were determined to correspond to average Pt particle sizes of  $\langle d \rangle_x = 3.9 \pm 0.5$ ,  $5.5 \pm 3.0$ ,  $5.6 \pm 2.0$ , and  $5.7 \pm 1.5$  nm, for x = 0.2, 1.0, 5.0, and 10 wt% Pt loadings, respectively. The particle size distributions were determined to be quite broad; they were used to estimate the fraction of Pt atoms on the surface, a parameter needed to estimate turnover numbers and turnover frequencies.<sup>30</sup>

The glycerol oxidation kinetic studies were carried out by using a 50 mL four-neck round-bottomed flask. The center neck was attached to an Allihn condenser connected to a ventilator, and all the other necks were plugged with rubber stoppers. Pure O<sub>2</sub> gas was bubbled into the mixture at atmospheric pressures through thin plastic tubes inserted into both left and right necks, and its flow was adjusted by using a flow meter. The flask was heated by using a hemispherical heating mantle, and the temperature was set by using a temperature controller connected to a thermocouple inserted into the mixture through the front neck. Designated amounts of glycerol, distilled and deionized H<sub>2</sub>O, and the catalyst were measured and introduced into the four-necked flask, typically 0.20 and 10.0 g of glycerol and water, respectively, and the appropriate amount of catalyst was added to reach the desired glycerol/Pt ratio, typically 500:1 (1000:1 was used for the studies *versus* Pt loading to better cover the wide range of catalytic surface available with the different catalysts). The system was assembled and heated to the designated temperature (typically 345 K), after which the O<sub>2</sub> flow (100 mL min<sup>-1</sup> unless otherwise indicated) was turned on and the timing of the reaction started. When the designated reaction time was reached, the O<sub>2</sub> flow was turned off, the heating removed, and the system cooled down using a water bath. After reaching room temperature, the flask was removed from the system and the mixture was filtered through a Buchner funnel and washed with distilled water. The solution and catalyst were collected separately.

The products in the solution were then analyzed by high-performance liquid chromatography (HPLC). The HPLC instrument consisted of an Altech 426 pump, a Rheodyne 7725i sample injector, an Agilent Zorbax SAX separation column, and a Linear UVIS 200 detector. Data were collected using a Tekpower TP4000ZC digital multimeter interfaced to a personal computer. A 2.5:1 mixture by volume of acetonitrile and phosphoric acid buffer containing  $5.8 \times 10^{-3}$  mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> and  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> NaOH in aqueous solution, for a final pH value of 2.2, was used as the eluent. The flow rate was set at 1 mL min<sup>-1</sup>, and detection was carried out at a



UV wavelength of 210 nm for most products and at 190 nm for GLY (and other non-absorbing molecules). Separate external standard calibrations were carried out to quantify the concentration of each product in the sample mixture and to determine the sensitivity limits: absorbents such as DHA and GLYALD could be seen at concentrations as low as  $1 \times 10^{-4}$  M, whereas the detection of GLY required the use of shorter excitation wavelengths ( $\lambda = 190$  instead of 210 nm) and showed approximately one order of magnitude lower sensitivity. Many other secondary products, including potential fragmentation products such as glycolic acid, acetic acid, lactic acid, and formic acid, were searched for but not detected; only four species were seen in the HPLC traces in all of our runs. In fact, the detected products reported here could always account for the consumption of GLY within a few percent of the total mass, the accumulated error range of our measurements.

Most of the kinetic data were acquired by carrying out individual runs to their end point and analyzing the reaction mixture afterward. In a few cases, additional samples were tested at intermediate times. During a typical sampling test, around 0.4 mL of the reaction mixture was taken out of the flask through a needle inserted in one of the rubber stoppers, immediately filtered by using a Millex-LG-0.20  $\mu\text{m}$  hydrophilic filter, and tightly sealed in a 0.5 dram (2 mL) vial. That aliquot was diluted to 50.00 mL with water using a volumetric flask, and if the pH value was not within the 2–7 range, the aliquot was neutralized or diluted to this designated pH range to avoid damage to the Zorbax SAX column. Typically, 100  $\mu\text{L}$  of the sample solution was injected into the HPLC system, and the measurement was repeated three times to get more accurate results. The concentration of a given product in the 50 mL solution was then calculated by using the appropriate standard calibration curve.

The following chemicals were purchased from commercial sources and used as provided: dihydrogen hexachloroplatinate(IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Alfa Aesar, 99.9% purity) and silica (aerosil, S5505, Sigma-Aldrich) for the catalyst preparation; glycerol (Sigma-Aldrich,  $\geq 99.5\%$ ) as the reactant; and acetonitrile (HPLC grade, Fisher Scientific), phosphoric acid (Alfa Aesar, 85 wt%), NaOH (pellets, Alfa Aesar, 98%), methanol (HPLC grade, Alfa Aesar, 99.8%+), 1,3-dihydroxyacetone dimer (TCI,  $> 96.0\%$ ), DL-glyceraldehyde dimer (Sigma-Aldrich,  $\geq 97.0\%$ ), DL-glyceric acid (20% in water, *ca.* 2 mol  $\text{L}^{-1}$ , TCI), formic acid (Alfa Aesar, 97%), glycolic acid (Alfa Aesar, 98%), lactic acid (1.0 N standardized solution, Alfa Aesar), tartronic acid (Alfa Aesar, 98%), pyruvic acid (Alfa Aesar, 98%), and sodium mesoxalate monohydrate (Sigma-Aldrich,  $\geq 98.0\%$ ) for the HPLC analysis and calibration.

### 3 Results

Fig. 2 displays data for a typical kinetic run of the glycerol oxidation catalytic process studied here, in this case for a reaction carried out at 343 K with the 1.0 wt% Pt/SiO<sub>2</sub>

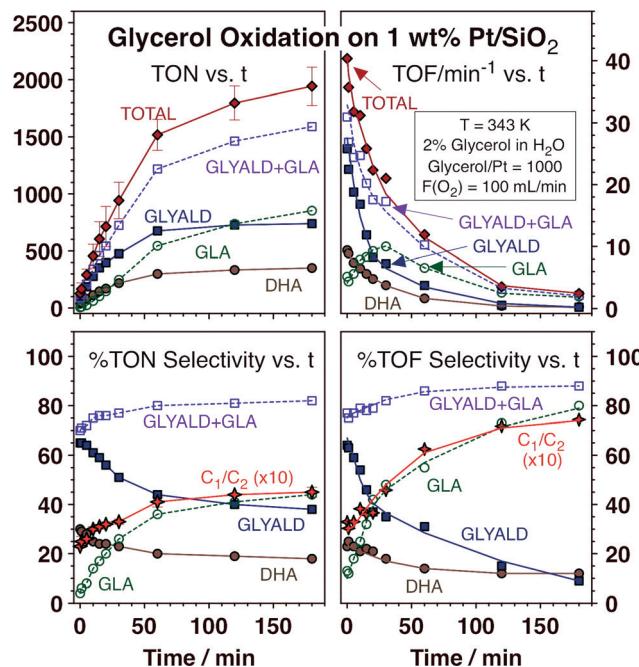


Fig. 2 Time-dependent kinetic data for the oxidation of glycerol with O<sub>2</sub> promoted by a 1 wt% Pt/SiO<sub>2</sub> catalyst. The following conditions were used for this run: T = 343 K, glycerol concentration = 2% in water, O<sub>2</sub> flux = 100 mL min<sup>-1</sup> (1 atm pressure), glycerol/Pt ratio = 1000. Top, left: Accumulation of the products, in the form of turnover numbers (TONs, GLY molecules converted per number of Pt surface atoms in the catalyst). Top, right: Turnover frequencies (TOFs, GLY molecules converted per number of Pt surface atoms in the catalyst per minute). Bottom, left: Selectivities based on accumulated products (TONs), in percentage of total products. Bottom, right: Selectivities based on TOFs, in percentage of total TOF.

catalyst. The top-left panel shows the accumulation of the different products detected in our batch reactor, plotted in the form of turnover numbers (TONs), expressed in units of glycerol molecules consumed per number of platinum surface atoms in the catalyst (estimated using the Pt nanoparticle size distributions obtained from TEM measurements), *versus* time. 95% confidence error bars are provided for the total conversion, estimated from statistical evaluation of five independent kinetic runs. Only three main products were seen in our kinetic runs, GLYALD, DHA, and GLA; no other compounds were detected within the detection limits of our experiments. This indicates no further conversion of the initial products, as has often been reported in other studies, likely because of the mild conditions used in our studies. The concentrations of the first two products, GLYALD and DHA, were seen to grow right from the start of the reaction, indicating their primary product character, whereas an induction period was seen for GLA, a secondary product from oxidation of GLYALD. These kinetic results also argue against the interconversion between GLYALD and DHA, a conclusion supported by the fact that the addition of DHA to the reaction mixture does not significantly alter the kinetics of the GLY conversion (see below, Fig. 7). It should be pointed out that the overall conversion appears to asymptotically reach a



TON value of about 500, equivalent to 50% conversion. This limit was observed in all runs reported here. The activity is ascribed to the supported Pt nanoparticles, since no activity is seen with silica alone.

The top-right panel of Fig. 2 displays the estimated turnover frequencies (TOFs) of the reaction, in units of glycerol molecules consumed per number of Pt surface atoms in the catalyst per minute, also as a function of reaction time. The TOFs were calculated from the slope of the TON *vs.* *t* traces provided in the left panel of Fig. 2. Most rates decrease rapidly in the initial stages of the reaction, except that for GLA, the TOF of which grows first until reaching a maximum at about 30 min and decreases again afterwards (a clear indication of its secondary product nature). The initial overall TOF in this catalytic run is about  $40 \text{ min}^{-1}$ , a value quite a bit higher than those seen with supported Pt catalysts in other reports<sup>15–18,20,27,29,31</sup> and also competitive with some Bi-modified samples<sup>15,16</sup> (Table 1). Since the conditions used in our study are milder than those in most past studies (*i.e.*, the temperatures are lower), we speculate that higher temperatures may lead to poisoning because of the decomposition of the reactants and/or products on the surface and the deposition of irreversibly bonded carbonaceous deposits on the metal.

The bottom two panels of Fig. 2 display the selectivities calculated from the TON (left) and TOF (right) plots *versus* time provided at the top. In addition to displaying the trends for the individual three main products detected here, namely, GLYALD, DHA, and GLA, two more traces are included in each panel for the combined selectivity for GLYALD + GLA and the ratio of oxidation products at the C<sub>1</sub> over C<sub>2</sub> carbon (C<sub>1</sub>/C<sub>2</sub>), used to highlight the stereoselectivity of the primary oxidation step. It is clear that there is an increase in selectivity for oxidation at the primary (terminal) carbons over time and also a gradual conversion of GLYALD to GLA (which points to the sequential nature of the conversion of GLY to GLYALD first and to GLA afterwards). Again, no obvious parallel primary reaction for GLA production is seen here, neither is any interconversion between GLYALD and DHA, as reported in other cases.<sup>4,14,17,32</sup> The trends seen for the TON

and TOF data in terms of selectivities are qualitatively the same, but the latter shows the effects discussed above more markedly.

The effect of temperature on the kinetics of the glycerol oxidation reaction is indicated by the data in Fig. 3. The left panel shows the TONs measured after 3 h of reaction with the same 1 wt% Pt/SiO<sub>2</sub> catalyst as before as a function of reaction temperature, in the range from 323 to 363 K, in Arrhenius form, whereas the right panel provides the results from analysis of the raw data in terms of selectivity. The range of temperatures studied here is quite narrow because of the experimental limitations imposed by the reaction but sufficient to highlight dramatic changes in kinetics. First, in terms of overall activity, there seems to be a sharp threshold around 333 K, below which the catalytic activity is almost undetectable. By 343 K, the catalytic conversion is already quite high, and because of the ~50% of conversion asymptotic limit mentioned before, no significant additional gains in activity were observed by increasing the temperature further. In exchange, selectivity toward GLYALD formation is quite high below 333 K but decreases as the reaction temperature is increased because of both competition with DHA production and further oxidation to GLA. A temperature of 343 K was chosen here for all subsequent experiments as a compromise between obtaining a reasonable activity and minimizing the loss of selectivity towards aldehyde formation.

The kinetics of the reaction is also affected by the initial concentrations of the reactants, as indicated by the data in Fig. 4. The dependence of the reaction rate on the concentration of GLY in solution is linear (Fig. 4, left), as expected for a first-order process. There is a slight loss of selectivity toward GLYALD production, even if the effect is not severe. By contrast, the rate of reaction goes down slightly with increasing oxygen flow (all experiments were carried out at atmospheric pressures, but the steady-state concentration of O<sub>2</sub> in the reaction solution is expected to kinetically reach different values with varying gas flow values). This may be explained by a possible partial oxidation of the metal surface. Early reports on this system claimed an increase in rate with increasing O<sub>2</sub> flow or pressure,<sup>19</sup> but others have seen

**Table 1** Literature survey of kinetic results for the oxidation of glycerol with Pt-based catalysts

Catalyst	Reaction conditions					Selectivities/%			Ref.
	T/K	O <sub>2</sub>	Glycerol/Pt	pH	TOF/min <sup>-1</sup>	GLYALD	GLA	DHA	
1 wt% Pt/C	323	3 atm	500	14.1	8.9 (0.25 h)	42			18
5 wt% Pt/C	333	1 atm, 150 mL min <sup>-1</sup>	425	~7	3.7 (20 min)	2	47	17	31
0.77 wt% Pt(111)-NC/CNT	333	1 atm	9000	~7	3.3	79	0.5	13	29
5 wt% Pt/C	393	1 bar, 300 mL min <sup>-1</sup>	1755	4	4.0				15
5 wt% 1 : 1 Pt + Bi/C	393	1 bar, 300 mL min <sup>-1</sup>	1755	4	8.7		21	51	15
5 wt% Pt/C	333	1 atm, 150 mL min <sup>-1</sup>	445	~7	0.58	3.0	70	2.8	27
5 wt% Pt/CNT	333	1 atm, 150 mL min <sup>-1</sup>	445	~7	0.87	3.8	60	3.9	27
5 wt% Pt/C	343	60 psi	135	7	3.2 (0–1 h)			12.9	16
3.6 wt% 5 : 1 Pt + Bi/C	343	60 psi	135	7	5.0 (0–1 h)			48.1	16
5 wt% Pt/C	333	1 atm, 150 mL min <sup>-1</sup>	100	~7	0.8 (0–6 h)	1.3	66.4	9.2	17
10 wt% 1 : 1 Pt + Bi/C	333	1 atm, 150 mL min <sup>-1</sup>	100	~7	1.1 (0–6 h)	0.0	5.4	49.0	17
0.5 wt% Pt/C	333	3 bar	2500	13.8	15		60	20	20
1 wt% Pt/SiO <sub>2</sub>	343	1 atm, 100 mL min <sup>-1</sup>	1000	~7	40	67	14	19	This work



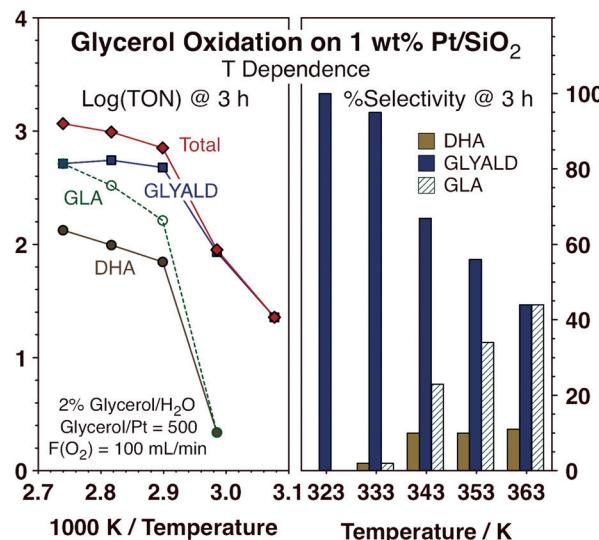


Fig. 3 Log(TON) after 3 hours of reaction versus  $1/T$  ( $T$  = reaction temperature) (left) and % selectivities of accumulated products after 3 h (right) for the conversion of glycerol on 1 wt% Pt/SiO<sub>2</sub> versus  $T$ . Reaction conditions: glycerol concentration = 2% in water, O<sub>2</sub> flux = 100 mL min<sup>-1</sup> (1 atm pressure), glycerol/Pt ratio = 500.

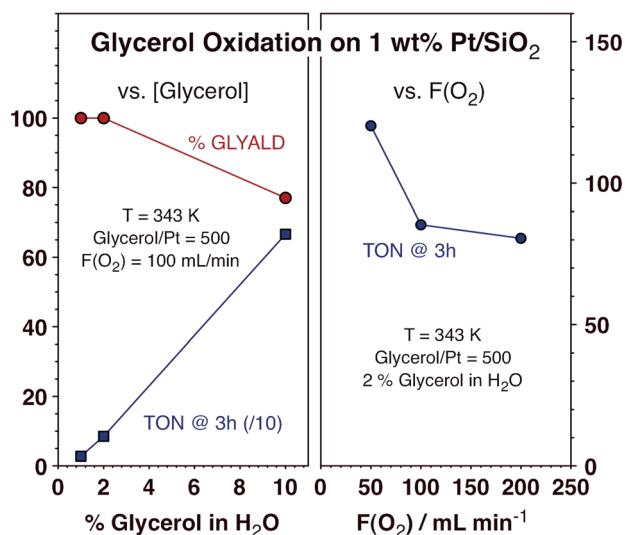


Fig. 4 TONs after 3 h (blue traces) and % GLYALD selectivity after 3 h (red) for the conversion of glycerol on 1 wt% Pt/SiO<sub>2</sub> as a function of glycerol concentration in water (left panel) and of oxygen flow at 1 atm (right). Reaction conditions:  $T$  = 343 K, glycerol/Pt ratio = 500; O<sub>2</sub> flux = 100 mL min<sup>-1</sup> for the data in the left panel; glycerol concentration = 2% in water for the right panel.

poisoning effects similar to that reported here.<sup>3,12</sup> An oxygen flow of 100 mL min<sup>-1</sup> was chosen for the remaining part of our kinetic work.

One key consideration in many catalytic reactions is the effect that the pretreatment used to activate the catalyst exerts on its performance. This was tested extensively in our investigation of the glycerol oxidation system. All catalysts were initially calcined to eliminate carbon contaminants, as

mentioned in the experimental details section, and then reduced in a hydrogen atmosphere to achieve optimal catalytic performance; much diminished activities were measured without the latter step. As indicated above, our catalysts displayed reasonable performance initially after such pretreatments, but their activity diminished with time, and conversion always stopped around 50%. Further experiments were designed to identify the cause of this poisoning. The data in Fig. 5 show results, in the form of TONs measured after 3 h of reaction at 343 K, from catalyst recycling tests where additional hydrogen treatments were carried out in between kinetic runs: after filtering the catalyst out of the reaction mixture from the first run and rinsing it with distilled water, exposure to hydrogen was carried out at the indicated temperatures ( $F(H_2)$  = 20 mL min<sup>-1</sup>, 3 h), and a second catalytic run was performed with a fresh reaction mixture. It was determined that, even without any catalyst treatments in between runs (other than the rinsing with distilled water), much of the initial activity is regained, even though activity had approached a value near zero in the first run (more on this below). This indicates that much of the catalyst poisoning is reversible, likely due to adsorbed DHA, which is rinsed away in between runs (see below). Moreover, almost all of the initial activity (and selectivity) could be recuperated by reduction of the catalyst at temperatures below 623 K. The activity with the recycled catalyst does decrease if the H<sub>2</sub> reduction is carried out at 673 K or higher temperatures, however. TEM images of the catalyst obtained after those treatments indicate that the changes are due to sintering of the supported Pt nanoparticles under such severe conditions (Fig. 6).

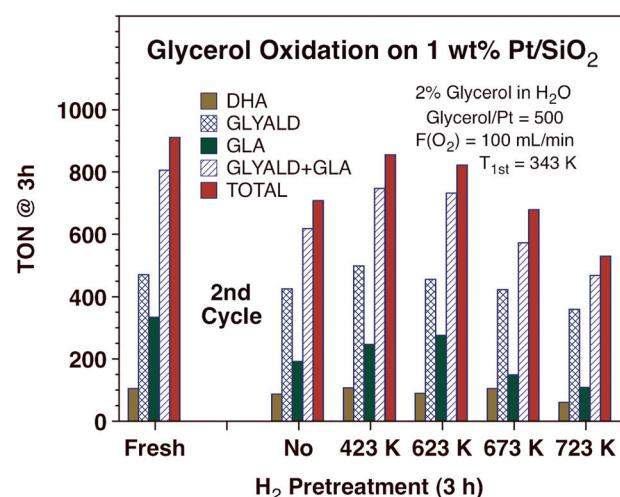


Fig. 5 TONs, total and for each primary product (DHA, GLYALD, GLA), after 3 hours of reaction for the conversion of glycerol on 1 wt% Pt/SiO<sub>2</sub>. Data are shown for a run with a fresh catalyst (left cluster) and with catalysts reused a second time after pretreatment in a H<sub>2</sub> atmosphere (3 h in 1 atm) at different temperatures. A set is also provided for the reused catalysts without any treatment in between runs (second cluster from the left). Reaction conditions:  $T$  = 343 K, glycerol concentration = 2% in water, O<sub>2</sub> flux = 100 mL min<sup>-1</sup> (1 atm pressure), glycerol/Pt ratio = 500.

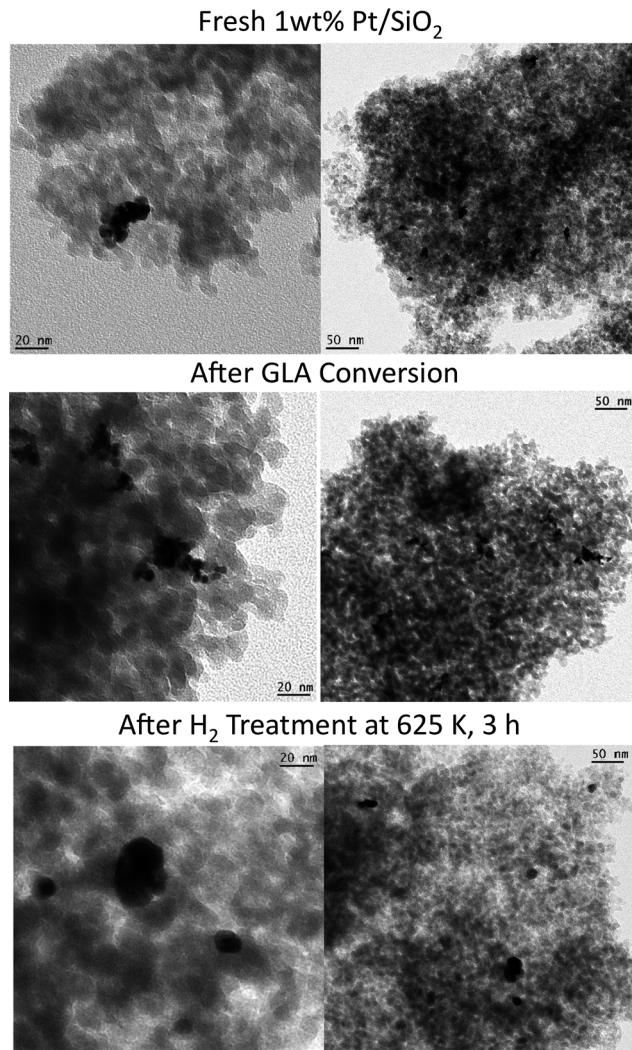


Fig. 6 Transmission electron microscopy (TEM) images of a typical 1 wt% Pt/SiO<sub>2</sub> catalyst before (top) and after (center) reaction and after treatment under a H<sub>2</sub> atmosphere at 625 K for 3 h. A significant amount of sintering is seen after the hydrogen treatment.

Results from additional recycling tests are presented in Fig. 7, in this case as a function of the type of treatment used. Kinetic data are provided from sequential runs with no treatment at all in between runs (except for the rinsing) and with pretreatments using H<sub>2</sub> alone or H<sub>2</sub> + O<sub>2</sub> combinations, all at 623 K (3 h). As before, a significant fraction, but not all, of the activity is regained by replacing the old reaction mixture with a fresh one, pointing once again to the reversible nature of most of the poisoning seen *versus* reaction time, and an additional loss of activity is also seen between the second and third runs. In this set of data, H<sub>2</sub> pretreatments in between runs led to a somewhat worse performance than without any treatment at all, but the addition of O<sub>2</sub> exposures also helped. Ultimately, the main conclusions from these experiments are that (1) much of the catalytic activity lost over time in the initial runs is regained by replacing the spent reactants with a fresh mixture and (2) some activity loss is irreversible, possibly because of metal

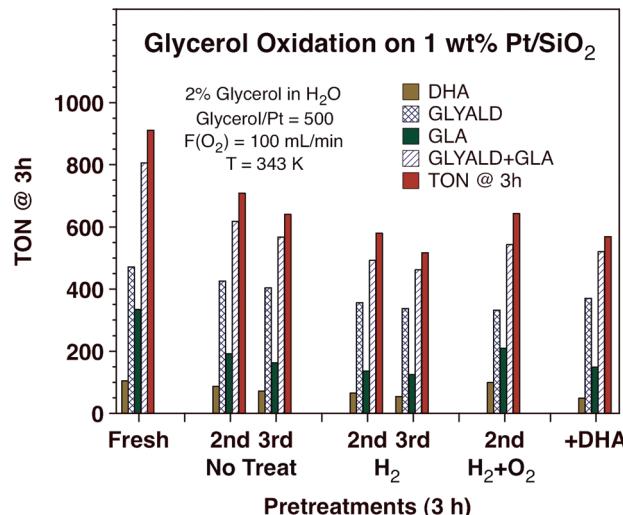


Fig. 7 TONs, total and for each primary product (DHA, GLYALD, GLA), after 3 hours of reaction for the conversion of glycerol on 1 wt% Pt/SiO<sub>2</sub>. Data are shown for a run with a fresh catalyst (left cluster) and with catalysts reused one or two more times after (from left to right): no treatment in between runs, pretreatment in a H<sub>2</sub> atmosphere (3 h in 1 atm) at T = 623 K, and after sequential H<sub>2</sub> and O<sub>2</sub> pretreatments at T = 623 K (3 h, 1 atm, each). The final set corresponds to a run with a fresh catalyst in which the reaction mixture was spiked with DHA (DHA/GLY = 0.08). Reaction conditions: T = 343 K, glycerol concentration = 2% in water, O<sub>2</sub> flux = 100 mL min<sup>-1</sup> (1 atm pressure), glycerol/Pt ratio = 500.

sintering and/or the growth of carbonaceous deposits on the surface. The explanation for the first of these observations seems to be poisoning of the catalyst by the competitive adsorption of DHA on its surface, since addition of DHA to the initial reaction mixture (DHA/GLY = 0.08) leads to similar losses in activity with a fresh catalyst as those seen after recycling (Fig. 7, far right data set). This poisoning does not seem to be highly selective, because the TOFs for the production of all GLYALD, DHA, and GLA are affected as a function of the extent of reaction. As far as we know, this DHA poisoning effect has not been reported before, but Wörz and coworkers have identified a similar poisoning exerted by GLA.<sup>14</sup> It is quite possible that several of the products, not only DHA, may act as poisons for this reaction.

Finally, the effect of metal loading on catalytic performance was briefly assessed. Our studies on the structure sensitivity of this reaction have led us to identify some interesting and complex features discussed in more detail in a separate publication,<sup>30</sup> but some data are presented here to place these effects in context with respect to those due to the extent of conversion of the reaction, the main point of the present report. Four catalysts were prepared with 0.2, 1.0, 5.0, and 10 wt% platinum loadings on the silica support by following the synthetic procedure described in the experimental details section. Fig. 8 displays the main kinetic data obtained with this set of catalysts. The two left panels, which show the overall TONs and TOFs measured as a function of time, indicate some differences among the different catalysts, with the



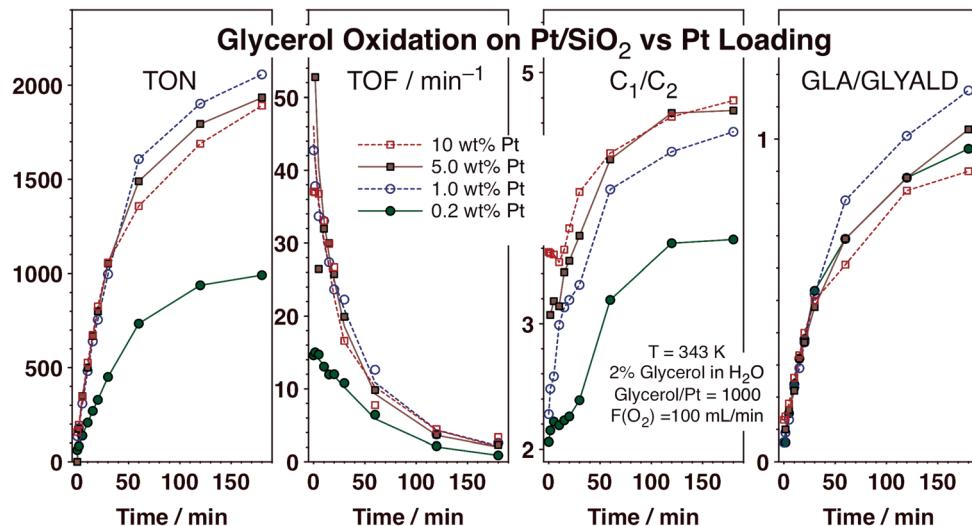


Fig. 8 Total TON (left panel), total TOF (in  $\text{min}^{-1}$ , second from the left),  $\text{C}_1/\text{C}_2$  selectivity ratio (second from the right) and GLA/GLYALD selectivity ratio (right) as a function of time, measured using four catalysts with varying loadings of Pt (0.2, 1.0, 5.0, and 10 wt%). Reaction conditions:  $T = 343$  K, glycerol concentration = 2% in water,  $\text{O}_2$  flux =  $100 \text{ mL min}^{-1}$  (1 atm pressure), glycerol/Pt ratio = 1000.

effective activity per Pt surface atom increasing with metal loading and therefore with particle size. In our past work, we have associated these changes to the requirement of large ensembles of Pt surface atoms for optimum glycerol adsorption and conversion.<sup>30</sup> Selectivity also depends on metal loading, as indicated by the two right panels of Fig. 8: larger loadings favor oxidation at the primary carbons and perhaps disfavor further oxidation of GLYALD to GLA. Notice, however, that these effects are somewhat masked by the changes seen as a function of conversion. It is this latter observation that we believe is worth highlighting from our work.

## 4 Discussion

The catalytic oxidation of glycerol is the key to several potential applications and has therefore been studied repeatedly in the past. Unfortunately, most reported work in this area is either incomplete or difficult to put in context. The early reports focused on reactions carried out under somewhat extreme conditions, in particular highly acidic or highly basic solutions, and emphasized deep conversion products.<sup>6–13,18</sup> More recent research has been carried out under greener conditions, at times using neutral water solutions, but even in those cases, the emphasis has often been in introducing new catalytic materials.<sup>1–5,14–17,19–24,27–29,31,33</sup> The vast majority of the reports on the catalytic oxidation of glycerol provide no, or limited, kinetic data.

Because of the lack of good-quality kinetic data, contrasting catalytic performance among the different catalysts put forward in the literature is difficult. We have made an attempt to summarize the available information for platinum-based catalysts in Table 1, even if the conditions used for the various reported experiments are significantly different. A few conclusions can be extracted from this data set. First, turnover numbers vary by more than an order of

magnitude depending on the catalyst and conditions used but are not clearly associated with specific types of samples or conditions: the highest TOFs are seen with regular Pt catalysts, without promotion, and the catalysts reported here (in our own work) promote the reaction at higher rates than the best past samples in spite of (or perhaps because of) the fact that we used milder reaction conditions (atmospheric  $\text{O}_2$  pressures, neutral pH). Second, initial selectivities are difficult to compare because they are often convoluted in the published reports: the ratio of oxidation at the primary alcohol position to that at the secondary alcohol position is rarely isolated from the selectivity between the production of the primary products (GLYALD and DHA) and those from subsequent oxidation steps. Nevertheless, it is clear that the addition of Bi to the Pt catalyst does switch the preference for the primary oxidation step, from ~2/3 of the yield being in the form of the oxidation of the primary alcohol(s) on pure Pt to the conversion of as much as half of the glycerol into DHA if Bi is added. Otherwise, no other clear selectivity trends can be extracted from the data, even though it seems that more extensive oxidation takes place under extreme pH conditions.

Here, we report on a series of kinetic trends, some of which corroborate previous observations. First, it was shown that the only primary products are GLYALD and DHA; GLA is produced *via* the sequential two-step oxidation of GLY *via* a GLYALD intermediate (Fig. 2). No support for the interconversion between GLYALD and DHA was obtained, in contrast with previous proposals from studies in non-neutral solutions.<sup>4,5</sup> The glycerol oxidation is activated, as expected, but the secondary conversion of GLYALD to GLA displays a higher activation energy than the initial steps to GLYALD and DHA, which means that multiple oxidation may be minimized at low temperatures (Fig. 3). The rate of glycerol conversion depends linearly on the concentration of GLY in the water solution, indicating simple first-order kinetics, but



shows a slight negative dependence on  $O_2$  flow rate (Fig. 4). Correlation of reaction rates with  $O_2$  pressure or flow is difficult in this case, mainly because  $O_2$  solubility may display a weak dependence on those parameters, but the negative order seen here is nevertheless likely to be significant and to indicate slight poisoning of the surface by the formation of a thin metal oxide layer (or a submonolayer of adsorbed atomic oxygen), as suggested before.<sup>12</sup> Presumably, the reason for the improvement in catalytic performance seen by alloying with gold may be related to the added resistance of the surface to oxidation.<sup>3</sup>

Perhaps the most important observation from our work is the strong changes in reaction selectivity observed as a function of the extent of conversion. As Fig. 2 highlights, not only the formation of GLA increases over time at the expense of the consumption of GLYALD, but also the selectivity of oxidation at the primary carbon atoms increases over time at the expense of oxidation at the central moiety: the  $C_1/C_2$  oxidation TOF ratio starts at only about 3 but increases to a value of ~8 towards the end of the catalytic runs. This is, as far as we can tell, a new observation. It is important because the changes in selectivity seen over the course of a given reaction are in many instances larger than those observed across experiments with different catalysts or conditions. This means that many studies reporting single conversion values at a fixed time may reach erroneous conclusions. For instance, there are clear trends in selectivity with Pt loading, with lower Pt loads favoring more secondary carbon oxidation (and perhaps accelerating GLYALD further oxidation), but those variations are less marked than the changes seen *versus* conversion time (Fig. 8).

The conversion dependence of the catalytic selectivities reported above is not due to further conversion of GLYALD, GLA, or DHA to secondary products, as has been reported in other cases,<sup>16</sup> since no detectable amounts of other products were ever seen in our experiments. Instead, our observation can be justified on the basis of poisoning of the surface by the products of the reaction, specifically by DHA. This explanation is supported by the evidence from recycling experiments collected in Fig. 5 and 7. First, it is clear that, although each individual batch reaction reaches a limit of conversion at approximately half of the initial amount of glycerol in the reaction mixture, after which the reaction stops, almost complete activity can be restored upon flushing of the old reaction mixture and its replacement with a fresh solution. The level of activity regained this way is approximately 80% of that seen in the first run when using the used catalysts as is, without any treatment in between runs (except water rinsing), but can reach almost 100% upon mild pre-hydrogenation at temperatures around 423 K (Fig. 5; more severe pretreatment conditions lead to Pt sintering and to an irreversible loss in activity). The new selectivity, in the second cycle of the reaction, is also close to that seen with the fresh catalyst, except perhaps for a slight increase in the ability of the used catalyst to promote the secondary oxidation of GLYALD to GLA. Further cycling of the catalyst does lead to a slow loss

of activity (Fig. 7), possibly because of the buildup of an irreversibly adsorbed carbonaceous layer, or even because of metal nanoparticle sintering, as mentioned before.

The poisoning effect of the DHA produced during GLY oxidation was tested directly by adding a small amount of DHA to the reaction mixture in experiments with a fresh catalyst. As indicated in Fig. 7, this leads to a loss of approximately 1/3 of the initial activity, a change akin to that seen with some of the reused catalysts. In addition, there seems to be a loss in selectivity toward the oxidation of the secondary carbon in GLY, even if the conversion of all products is poisoned by this DHA addition: the selectivity for the oxidation of the terminal alcohol groups reaches ~90%. Our conversion-dependent results explain the change in selectivity reported in early studies with the type of reactor used (batch *versus* continuous flow):<sup>6,9</sup> both total activity and selectivity toward DHA were improved with a fix-bed reactor, compared to the results from a batch reactor, presumably because in the latter the accumulation of DHA in the reaction mixture poisons the appropriate reaction sites. Quite likely, sites that favor oxidation at the central carbon position get blocked selectively by adsorbed DHA. It should be noted that such selectivity is not absolute, since DHA does poison GLYALD and GLA production as well, and that the use of flow reactors may minimize but not fully avoid the slowing down of the reaction over time, because a slow irreversible buildup of residues on the surface of the catalyst cannot be avoided. Nevertheless, the inhibition of catalytic performance because of DHA accumulation in the reaction mixture is quite significant and may dominate the kinetics measured for glycerol conversion in batch reactors. In more general terms, one of the main conclusions of our work is that comparisons of catalysts for glycerol oxidation in terms of activity and selectivity need to take into account the temporal evolution of the reaction. In addition, an effective catalytic process may require a continuous flow design, especially if the goal is to produce DHA preferentially.

## 5 Conclusions

The kinetics of oxidation of glycerol in water promoted by silica-supported platinum catalysts was studied in some detail. The accumulation of the main primary products, namely, DHA, GLYALD, and GLA, was followed over time, and turnover frequencies (TOFs) and selectivities, in the form of  $C_1/C_2$  as the initial oxidation position and of GLA/GLYALD ratios, were calculated as a function of the time of reaction and overall conversion. The kinetics measured in our experiments are consistent with the competitive initial oxidation of alcohol groups at the primary (terminal) *versus* secondary (central) carbons, to produce GLYALD and DHA, respectively, and with the subsequent oxidation of GLYALD to GLA; possible  $GLYALD \leftrightarrow DHA$  interconversion or GLA formation from DHA is inconsistent with the time evolution of the products measured here as well as with the kinetics obtained with reaction mixtures that include DHA. Both  $C_1/C_2$  and GLA/



GLYALD selectivities were seen to change with reaction time, the first from an initial value of approximately 3 to a final ratio of ~8 after about 50% conversion, the limit reached in all runs. All reactions are activated, and measurable conversions were seen only at temperatures of 333 K and above. Oxidation of GLYALD to GLA requires higher temperatures, at which point a decrease in selectivity toward GLYALD (*versus* DHA) production is also observed. Total TOFs were seen to depend linearly on the concentration of glycerol in the aqueous solution but to decrease slightly with increasing O<sub>2</sub> flow into the reaction mixture.

Extensive studies were carried out to evaluate the recyclability of the catalyst. Approximately 80% of the initial activity could be recuperated simply by replacing the spent reaction mixture with a fresh one, and almost full performance could be reached if the used catalyst was pretreated in H<sub>2</sub> at 423 K in between runs. On the other hand, treatments of the catalyst in between runs at higher temperatures, with H<sub>2</sub> alone or with sequential H<sub>2</sub> and O<sub>2</sub> atmospheres, lead to the irreversible partial loss of activity due to sintering (as corroborated by electron microscopy). Addition of DHA to the reaction mixture also leads to decreases in catalytic activity and selectivity toward DHA production, a result that indicates the poisoning effect of the accumulation of products, DHA in particular, in the reaction mixture. Finally, the performance of Pt/SiO<sub>2</sub> catalysts was briefly tested as a function of metal loading. In general, lower Pt loadings lead to lower total activities, to higher selectivities toward oxidation at the central carbon position, and to faster secondary oxidation of GLYALD to GLA. However, all these trends are more subtle than those related to the extent of conversion. Further studies on the effect of Pt nanoparticle size and shape on the performance of these catalysts for the oxidation of glycerol were published elsewhere.<sup>30</sup>

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