



# Palladium catalysed oxidation of glycerol—Effect of catalyst support



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## ABSTRACT

The activity and selectivity of Palladium catalysts on various supports, for the liquid-phase oxidation of glycerol in basic condition, have been studied. Activated carbon (AC), SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were the supports studied. The catalysts were characterized using a variety of techniques (TEM, BET, Pulse-Chemisorption, TPD, TPR and XPS). The support is shown to have a significant effect on both rate and selectivity of the reaction, with the best rate of glycerol conversion, as well as selectivity to glyceric acid, being obtained for activated carbon (AC) among all the supports studied. The results have been interpreted in terms of known concepts of metal-support interactions. It is concluded that the electronic interactions between the metal and support, as well as acidic/basic properties of catalyst, play a vital role in product selectivity and activity.

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## 1. Introduction

Concomitantly with the interest in biodiesel in the last two decades, studies on ways to upgrade glycerol, the major byproduct of biodiesel production, have also intensified. The yield of glycerol in biodiesel production is about 10% by weight. A surplus of glycerol is therefore expected to hit the market, as biodiesel gains ground as a transportation fuel, because of its renewable, and relatively environment-friendly nature. While a number of target products from glycerol can be envisioned, given the price volatility of glycerol, there is a view that targeting high-value, low-volume chemicals through oxidative routes may be the more attractive option [1–3]. Heterogeneous catalytic oxidation of glycerol has therefore attracted considerable attention in recent years. Such oxidations are usually non selective, and this has always been a challenge for reaction engineers when it comes to selectivity engineering. Interventions at the micro level (mainly through the use of selective catalysts) and the macro level (via reactor design) have been the usual approaches to tackle this problem. Of these, catalysis research is the one that holds by far the greater potential. The search for a catalyst should not confine itself to catalytically active species alone, but should also consider issues such as the support and its possible role in modifying the effect of the catalyst, how amenable the supported catalyst is for use in industrial reactors and so on.

Glycerol oxidation proceeds by a complex mechanism and leads to a multitude of products, and different possible schemes have been reported in the Refs. [2–7]. It has been shown [2,8,9] that, by tuning the reaction conditions (especially pH), and with appropriate catalysts, one can direct the oxidation to different product profiles. Thus, under acidic conditions and with bismuth catalyst (either independently or in combination), the secondary alcoholic group can be preferentially oxidized to obtain dihydroxyacetone (and hydroxy-pyruvic acid), whereas under basic conditions and with Platinum group catalysts or gold, the reaction yields glyceric acid and tartronic acid as the main products. In this paper, we concern ourselves with oxidation under basic conditions. Hirasawa et al. [10] describe some ways of directing the reaction towards dihydroxyacetone.

The mechanism of glycerol oxidation under basic conditions over heterogeneous catalysts has been the object of several studies in the literature. A high pH is required for the initial de-protonation of glycerol and subsequent dehydrogenation to glyceraldehyde, which then undergoes further oxidation to glyceric acid [3–5,11–13]. According to some theoretical and experimental studies [3,9], the reaction involves steps on the catalyst surface as well as in solution. Di-oxygen is only indirectly involved in the oxidation, through its participation in the recycling of the hydroxyl species. Researchers have also observed peroxide formation during glycerol oxidation and commented on peroxide formation as the probable reason for C–C cleavage and formation of lower carbon products such as glycolic and formic acids [7,13–17].

The catalysts, which have mainly attracted attention in the context of glycerol oxidation under basic conditions, are Pd, Pt, Au and their combinations, with various supports and promoters

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[1,4,5,8,12,13,18–25]. There is a view [2,9] that gold is more stable against deactivation and leaching as compared to Pt and Pd, but some results [9] show a higher incidence of C–C scission byproducts forming with gold catalysts, possibly due to the high acidity of some of the catalysts studied [2]. Pt and Pd catalysts also have the advantage of being active under acidic as well as alkaline conditions, while Au is active only under alkaline conditions. The activity and selectivity of the catalyst are not only influenced by the active phase, but also by the metal particle size, the support and its interaction with the active phase. Recent reviews by Katryniok et al. [2] and Davis et al. [3] provide good overviews.

While the importance of the support effect in the catalyst engineering for glycerol oxidation has been recognized [2], it is only recently that extensive studies are starting to emerge. In general, interaction of the metal with the support can lead to a better or a worse performance of the catalyst, and hence is important to understand properly. Furthermore, these effects depend not only on the nature of the support, but also on the method of catalyst synthesis since the latter determines the nature of the forces that bind the metal to the support [26–33]. Much of the literature available on glycerol oxidation focuses on various forms of carbon as the support and studies on other supports are few. Carbon has the advantage of being stable in both acidic and basic media [34] and that makes it attractive for glycerol oxidation, which exhibits different product profiles under the two sets of conditions. Further, recovery of the active metal from the spent catalyst is easy since the support can be burned off.

The effect of support in glycerol oxidation has been studied mainly for gold-based active metal catalysts [11,35–38], and studies on palladium catalysts on different supports are few. Most of the available studies use a carbon support. The studies are at temperatures of 50–60 °C, and cover a wide range of oxygen pressures. It is clear from these studies that use of Pd catalyst leads to the same products as gold, but the selectivities vary. The early studies of Garcia et al. [1] showed that a high pH increased the activity as well as selectivity to glyceric acid with Pd/C catalysts. These authors conducted their reactions at atmospheric pressure with a continuous flow of air, and the reaction at pH 11 was fast enough that the process became limited by external mass transfer (as shown by their measurements of dissolved oxygen). Under such conditions, they report a maximum selectivity to glyceric acid, of about 70% at 100% conversion of glycerol. Following upon the findings of Garcia et al. [1], subsequent literature on the palladium catalysis of glycerol oxidation has tended to focus on high oxygen partial pressures, and high pH. Important examples are Gallezot et al. [39], Prati et al. [21–23,40], Ketchie et al. [13] and Carrettin et al. [19].

Influence of the metal particle size on the catalyst activity and selectivity has been a focus in several studies [14,22]. With Pd catalysts, Prati et al. [22] found that the selectivity towards glyceric acid increases with an increase in particle size while catalytic activity and selectivity towards tartronic and glycolic acid decrease. These differences were observed for sizes of 10–15 nm, while in the range of 2–10 nm, particle size did not seem to matter. These findings may be compared with findings of Ketchie et al. [14] on gold catalysts that the smaller the nanoparticles, the higher the activity, but the lesser the selectivity to C3 products. While considering the particle size effect, one has to also factor in the possibility that very fine particles are more easily leached out as compared to the larger particles [2].

While, as noted above, several aspects of supported metal catalysts have attracted attention in the literature, one aspect that is inadequately dealt with in general, is the issue of transport limitations [2]. Many inferences linking catalyst characteristics to their performance become questionable in the absence of a satisfactory demonstration of the absence of transport limitations in the reaction studies. There is evidence in the literature of a reduction in

the rate [10,35] and a loss in selectivity [41] with an increase in micro-porosity. The importance of choosing the conditions of catalyst evaluation with an adequate appreciation of possible transport limitations is therefore underlined.

In the present work, we focus on palladium-catalyzed glycerol oxidation in basic conditions. The main objective of the study, apart from establishing the kinetics and selectivity of different catalyst systems, is to understand the influence of the support, and hence several catalyst supports – activated Carbon, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> – have been employed in the studies. As mentioned above, activated carbon supported catalysts have been studied more than others for glycerol oxidation, and therefore provide a benchmark for the performance of other supported catalysts. Alumina and silica are among the most prevalent supports for metal catalysts. While the use of alkaline conditions calls into question the physical stability of the silica-supported catalyst, we nevertheless thought that it would be interesting to include it in our study for the following reasons: (i) in terms of acidity/basicity, and metal-support interaction (which are likely to be important in the performance of the catalyst [38]), the inclusion of silica support provides for a range of conditions to be studied, and (ii) conservative estimates of the dissolution rate (see Niibori et al. [41] for example) show that the dissolution within the timescales of our experiments is likely to be very small; in any case, activity comparisons would be based on initial rates. The choice of TiO<sub>2</sub> was because, in general (though not for glycerol oxidation), much of the information that is available on metal-support interaction for Pd catalysts is for this support [32,33,42–45]. Characterization techniques such as TEM, Temperature-programmed techniques (Desorption, reduction and oxidation), Pulse-chemisorption, XPS and BET (Surface area and porosity) have been used to understand possible support effects. Finally, reactions have been conducted under conditions of kinetic control and attempts have been made to relate catalyst/support characteristics to activity and selectivity.

## 2. Experimental methods

### 2.1. Catalyst preparation

Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> were obtained from Vineeth Chemicals and Pd/AC, from Merck Chemicals. Pd on TiO<sub>2</sub> was synthesized as part of this work, by impregnation method with chemical reduction [46]. In a typical preparation, an aqueous solution of PdCl<sub>2</sub> (99.99% Merck Chemicals) according to the required weight percentage was added to a slurry of TiO<sub>2</sub> (99.9% Rutile, Wilson Laboratories, India) under agitation, and stirring was continued for 2 h. A solution of KOH + sodium borohydride (99.99%, Merck Chemicals) was then added over 2hr, small aliquots at a time, to complete the chemical reduction. After chemical reduction, the catalyst was filtered and washed with milli-Q water. The catalyst was then dried at 120 °C for 12 h followed by calcination at 500 °C in an inert atmosphere.

### 2.2. Catalyst characterization

The catalysts were characterized using TEM, BET, XPS, temperature programmed adsorption/reduction and pulse-chemisorption. TEM analyses of catalyst were carried out with Philips' model CM200 and Jeol JEM 2100F instruments in order to study the size distribution of palladium crystallites. Pore size distribution and surface area were measured by BET method (Micromeritics ASAP 2020). Before subjecting to BET analysis, the catalysts were pretreated by degassing in an inert atmosphere at 300 °C.

To determine the binding energies and oxidation state of palladium, X-ray photoelectron spectroscopy (XPS) was carried out (ThermoVG Scientific A1214). Samples were prepared by

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