Accepted Manuscript

Title: Palladium catalysed oxidation of glycerol –Effect of catalyst support

Author: Ashutosh Namdeo S.M. Mahajani A.K Suresh



Please cite this article as: Ashutosh Namdeo, S.M.Mahajani, A.K Suresh, Palladium catalysed oxidation of glycerol –Effect of catalyst support, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.05.008

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Palladium catalysed oxidation of glycerol -

Effect of catalyst support

Ashutosh Namdeo, S.M. Mahajani and A.K Suresh*

Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai, India 400076

^{*}Corresponding author : aksuresh@iitb.ac.in

Graphical Abstract



Highlights

- The effect of support on Pd catalyst has been studied for glycerol oxidation.
- Metal-support interaction has been probed through XPS and other techniques.
- Carbon-supported Pd was more active and selective than oxide supported Pd.
- Support effect was less for the carbon support as compared to oxide supports.
- Electronic interaction and support acidity have been identified as key factors.

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), SiO₂, Al₂O₃ and TiO₂ 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.

Keywords

Oxidation; Glycerol; Catalyst Support; Selectivity; Palladium

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 literature[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 deprotonation 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[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 $50-60^{\circ}$ 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, SiO₂, Al₂O₃ and TiO₂ - 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 TiO₂ 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/SiO₂ and Pd/Al₂O₃ were obtained from Vineeth Chemicals and Pd/AC, from Merck Chemicals. Pd on TiO₂ was synthesized as part of this work, by impregnation method with chemical reduction[46]. In a typical preparation, an aqueous solution of PdCl₂ (99.99% Merck Chemicals) according to the required weight percentage was added to a slurry of TiO₂ (99.9% Rutile, Wilson Laboratories, India) under agitation, and stirring was continued for 2 hrs. 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^{0} C for 12 hours followed by calcination at 500^{0} 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 dispersing the catalyst powders on an aluminum foil. The working pressure of Argon in the analysis chamber was less than 1.5×10^{-7} Pa. A monochromatic Al K- α source was used. The kinetic energies obtained which were converted to binding energies using 0.5 eV as spectrometer correction, using the equation: BE (eV) = (1486.6 - KE) + 0.5.For Pd/SiO₂, Pd/Al₂O₃ and Pd/TiO₂; C_{1s} (284.6 eV) was used as an internal calibration. For Pd/AC, Ag dot was used for internal calibration (standard Ag3d_{5/2} peak position is 368.2 eV).

To study the support interaction and dispersion, temperature programmed desorption and reduction (CO-TPD, TPR) and pulse-chemisorption techniques were used (TPDRO 1100, Thermo Scientific). In a typical pretreatment procedure, the gas line was first cleaned by inert gas (Argon), and then the sample was exposed to 5% O_2 /He followed by 5% H_2 /Ar to ensure that the exposed catalyst surface is first oxidized and then reduced completely. Finally, a high temperature desorption was carried out by the inert gas argon. This ensures that the active metal surface of the catalyst is at zero oxidation state and the catalyst is free from any impurities.

After pretreatment, Pulse chemisorption and Temperature programmed desorption (TPD) were carried out on the same sample. Pulse chemisorption studies were carried out by sending a known number of calibrated pulses of CO. After chemisorption, the sample, now saturated with CO, was used for TPD analysis. In the case of TPO/TPR, the catalysts were pretreated (as above) and then TPO followed by TPR were performed.

Pyridine-TPD and CO_2 pulse chemisorption were performed to determine the acidity and alkalinity of oxide supports. Further, to know the nature of acidic sites of oxide supports, FTIR (MAGNA 550, Nicolet Instruments Corporation, USA) spectroscopy was carried out using pyridine as a probe molecule. All the catalyst samples were first treated with pyridine and then kept for 12 hours at $120^{\circ}C$ under an inert atmosphere to remove all physisorbed pyridine, and the samples were then used for FTIR and TPD measurements. The alkalinity of the catalysts was determined by CO_2 pulse studies, carried out in a manner similar to CO pulse-chemisorption studies.

2.3 Reaction studies

Experiments on the oxidation of glycerol were performed in a 100 ml steel autoclave (Sharad Autoclave). The reactor assembly is shown in Figure 1. The autoclave was equipped with a pressure gauge, pressure sensor, heater, automatic cooling, temperature control and drive for agitation. Typically, the autoclave is charged with the required concentration of glycerol in water (Milli-Q water purged with N₂). NaOH (99.9 % Merck) and fresh catalyst (Pd/AC, Pd/SiO₂, Al₂O₃ and Pd/TiO₂) are added according to the required ratio with glycerol for every run. Initially, the mixture is stirred at low RPM (100 RPM) and heated up to the required temperature in Nitrogen (99.99% Med-Gas) atmosphere. Once the required temperature is attained, the nitrogen in the autoclave is flushed out with oxygen, the autoclave is pressurized with oxygen

(99.99% Med-Gas), and the speed of agitation is increased to the desired level. A constant oxygen pressure is maintained in the reactor throughout the experiment.



Figure 1: Oxidation reaction setup

The following conditions were kept the same in all the experiments: Temperature= 60° C, Pressure=6 Bar; Glycerol/Metal (Pd) = 1000 (mol/mol); NaOH/Glycerol=4 (mol/mol); RPM= 800, reaction volume= 60 ml, reactant (glycerol) concentration = 0.6 molar.

The particle size and stirrer speed were chosen so as to eliminate the possibility of any transport limitations (external or internal), based on preliminary experiments. The conversion-time profiles as well as product profiles were found to be independent of stirrer speed for stirrer speeds greater than 800 RPM. Calculations based on Weisz-Prater criterion (for example, as carried out by[47], see the Supplementary Material (SM) for details) showed that internal transport limitations were

absent for catalyst particle sizes of 5 microns (with the estimated W-P parameter being significantly less than 0.3).

Quantitative analysis of reaction mixtures was carried out on a Waters High Performance Liquid Chromatograph (HPLC) equipped with UV and RI detectors. Calibration standards such as glycerol (98%), dihydroxyacetone (98%), acetic acid, formic acid, glycolic acid (70% in water), and oxalic acid (98%), were obtained from Merck. Tartronic acid (97%), glyceric acid calcium salt dihydrate (99%) and glyceraldehyde (98%) were obtained from Sigma Aldrich. Hydroxypyruvic acid sodium salt (99%) and glyoxalic acid (50% in water) were obtained from Himedia and Spectrochem (India) respectively. An Aminex HPX-87H (Bio-Rad) column was used for analysis at 60° C, with a mobile phase flow rate of 0.6 ml/min. The mobile phase, 5mM of H₂SO₄ in water/acetonitrile was made in the following manner. 300 ml of acetonitrile was taken in a 1000 ml of volumetric flask and 10 ml of 0.5 molar H₂SO₄ was added. The solution was made up to 1000 ml with milli-Q water. This mobile phase was degassed in a sonicator for at least 2 hours before use.

For each component of interest, calibrations were prepared by plotting the area under the peak (peak height in the case of overlapping peaks) vs. concentration. Reaction samples were filtered before analysis using a 0.2-micron filter, and neutralized by adding a known amount of H_2SO_4 . Based on the calibrations, the concentrations of reactant and products were obtained and selectivity and conversion calculated (See supplementary material for more details).

3. Results and discussion

3.1 Pore size distribution and surface area

In view of the fact that intra-particle diffusion limitation can make a significant difference in activity and selectivity, we have performed BET for pore size distribution and surface area analysis. Table 1 summarizes the results. An analysis of the results using t-plots and BJH theory[48] showed that Pd/TiO₂, unlike the other catalysts studied (Pd/SiO₂, Pd/Al₂O₃ and Pd/AC), had very low porosity with most of the measured surface area coming from the external surface. Pd/SiO₂ and Pd/Al₂O₃ showed a significant contribution from meso-pores with negligible micro-porosity, while Pd/AC had significant micro-porosity. As discussed above, C-C cleavage and loss in activity have been observed in microporous catalysts[11,35,49]. Because of the absence of micro-porosity in oxide supports internal diffusion is unlikely to limit the rate. As mentioned above, our calculation of Weisz-Prater criteria shows no likelihood of internal diffusion effects even for Pd/AC although micro-porosity is significant.

Catalyst	BET surface area m ² g ⁻¹	Pore diameter $(A^{\theta}, BJH theory)$	Pore width $(A^0, BET$ theory)	Total pore volume(cm ³ g ⁻¹)	t-plot micro- pore volume (cm ³ g ⁻¹)
Pd/AC	1500	42	23	0.92	0.38
Pd/SiO ₂	250	88	94	0.59	0.012
Pd/Al_2O_3	280	47	51	0.36	0.018
Pd/TiO ₂	2.8	184	94	0.0065	0.00015

Table 1: Results of BET characterization of the catalysts used

3.2 Crystallite size

Crystallite sizes were determined from transmission electron micrographs as well as inferred from pulse chemisorption studies. The TEM images of the catalysts are shown in Figures 2-5, which indicate similar Pd particle sizes dispersed on the support in all cases, with an average diameter of 4-7 nm.



Fig 2: TEM images of Pd on AC showing crystallite size distribution of Pd on the support



Fig 3: TEM images of Pd/SiO₂ showing Crystallite size Distribution of Pd on the support



Fig 4: TEM images of Pd/Al₂O₃ showing crystallite size distribution of Pd on the support



Fig 5: TEM images of Pd/TiO_2 showing crystallite size distribution of Pd on the support

The CO Pulse-chemisorption results are shown in Table 2. While particle sizes derived from pulse studies agree reasonably with those from TEM for Pd/AC, they are seen to be different for the other catalysts. These calculations assume a 1:1 stoichiometry for chemisorption of CO on Pd. Supported Pd catalysts often show evidence of more than one type of adsorbed CO: a linearly bonded CO as well as multiply co-ordinated (or bridge-bonded) CO[50–52] (see below under TPD for further discussion on this). In fact, recognizing this, the TPDRO software uses a default stoichiometry of 1.5 (atoms of Pd per atom of CO), which gives a metal particle size of 7 nm for Pd/AC. CO adsorption can also be reduced because of metal-support interaction, resulting from a decoration of the metal particle by the oxide and/or from electronic interactions[53]. A strong interaction between the metal and the support causes a reduction in the extent of CO adsorption, thus over-estimating the size of metal particle. Literature[50,51] suggests that chemisorption cannot be depended on for dispersion calculations in such cases, and hence, we have used the TEM-based dispersion values in our calculations of TOF. On the basis of TEM results, it is seen that the metal particle sizes for the different preparations used are comparable, and further, are in a range where significant dependence of performance on metal particle size is not expected. Any difference in performance between the different catalysts has therefore to be explained on a basis other than particle size.

Table 2: Values of Dispersion based on TEM crystallite size of palladium and CO- Adsorption values from pulse-chemisorption studies. (Average particle sizes estimated from pulse-chemisorption are shown for comparison)

Catalysts	CO Adsorption	Ds	Ds*	Percentage
	NCO _{Ad}			dispersion #
	(µmol/g of Pd)	nm	nm	(PDT)%
Pd/AC	57.15	9	6	19.23
Pd/SiO ₂	22.87	23	9	13.67
Pd/Al_2O_3	21.61	25	8	14.38
Pd/TiO ₂	20.07	26	7	17

 NCO_{Ad} \rightarrow Normalized based on palladium content

 $Ds \rightarrow Surface$ -weighted average Diameter calculated from pulse-chemisorption

 $Ds^* \rightarrow Calculated from TEM images$

#PDT \rightarrow Percentage dispersion calculated based on the obtained TEM particle size of the palladium dispersed on the catalysts

3.3 TPD, TPO and TPR

TPD results for the catalysts are shown in Fig. 6. According to the literature on CO adsorption on Pd metal[54–56], a desorption temperature in the range of 100-200⁰C is expected. For the supported catalysts of our interest however, we observed significant differences from this range depending on the support. In the case of Pd/AC, we observe a broad desorption peak, but desorption starts at a relatively low temperature, as expected of linearly adsorbed CO (PdCO). For all the oxide supports, the desorption peaks occur at much higher temperatures, with the peak positions corresponding to bridge bonded CO (Pd₂CO), which generally desorbs at temperatures greater than 250°C[52,57]. For Pd/SiO₂, desorption starts at around 440°C with the peak at 624[°]C. For Pd/Al₂O₃, desorption starts at about 530[°]C and peaks at 650[°]C. For Pd/TiO₂ two peaks are seen; the first peak occurs at a temperature roughly similar to the case of SiO₂, whereas the second occurs at about 750° C. This second peak in the case of TiO₂ is probably due to a spillover of oxygen from the TiO₂ lattice, which combines with the adsorbed CO to form $CO_{2}[58]$. Alternatively, it may also be due to the decomposition of adsorbed CO on the catalyst surface into adsorbed carbon and $CO_2[54,57]$. A similar profile for Pd/TiO₂ has been reported by Dropsch et al. [52], who confirmed the formation of CO_2 at high temperatures by TPD-MS.



Figure 6: TPD profile of Pd/AC, Pd/SiO₂, Pd/Al₂O₃ and Pd/TiO₂

The high desorption temperatures in the case of oxide supports are indicative of a high degree of metal-support interaction. Dropsch et al.[52] concluded from their studies that the strength of interaction between Pd metal and support increases with increasing ionic character of the support $(SiO_2 < Al_2O_3 < TiO_2)$. A strong support interaction, in addition to causing a shift in the desorption temperature, results in a decrease in the extent of carbon monoxide adsorption[53,54].Our results

are broadly in support of this; it may also be seen that the discrepancies between TEM and chemisorption results for metal particle size (discussed earlier) are in the same order as the shift in desorption peak temperatures for alumina and silica supports. From the TPD results, the TiO₂ case seems qualitatively different from the others. Benvenutti et al.[53], who carried out an FTIR study of hydrogen and carbon monoxide adsorption on Pt/TiO₂, Pt/ZrO₂, and Pt/Al₂O₃ found that the carbonyl band shifts to lower wave numbers, as a consequence of the presence of hydrogen on the support, possibly at the metal-support interface, and consequent electronic interactions[53]. They also interpret their results as indicative of strong metal-support electronic interaction.

TPO studies were carried out on all catalysts except for Pd/AC, in whose case the possibility of combustion of the support precludes such a study. Oxygen consumption peaks were observed at 366^{0} C, 331^{0} C and 307^{0} C for Pd/Al₂O₃, Pd/TiO₂ and Pd/SiO₂ respectively, showing that the alumina support renders the oxidation of Pd more difficult as compared to the other two oxide supports. Oxygen consumptions were determined from the peak areas and gave a consumption of about 1 mol/mol Pd in the case of Pd/Al₂O₃, and much higher values for the other cases, suggesting single/multi-layer adsorption in addition to reaction in these cases.

Results from our TPR studies (conducted immediately following TPO; results not shown) showed a strong negative peak (hydrogen evolution) at a low temperature (below 100° C). This has also been observed by other research groups (Shen et al.[54] and references therein[59–61]), and is due to decomposition of Pd_xH_y; Palladium has a propensity to form hydrides even at room temperature[54], and the low temperature hydrogen evolution is due to the decomposition of

these species. The occurrence of this peak makes it difficult to detect any consumption peaks which follow either at similar or at nearby temperatures in the case of oxide supports. Distinct hydrogen consumption peaks were only observed at much higher temperatures (above 350° C) which are due to reduction of oxide supports[29,62–64].

Electronic interaction between the metal and support is usually a major factor in such cases[31]and XPS is a convenient tool to get an insight into this. The support may also influence the catalytic activity due to other reasons such as its acidic/basic nature (see for example Gross et al.[28] on CO and CO₂ hydrogenation), and this will also be investigated in the following sections.

3.4 XPS Analysis

XPS results for the four catalysts used in this work are shown in Figure 7. Peaks were observed for each catalyst corresponding to $Pd3d_{5/2}$ and $Pd3d_{3/2}$. Palladium peaks were obtained by Pd3d spectra fitting of raw data with Gauss-Lorentz curve after subtraction of Shirley background using XPSPEAK4.1 software[65]. While fitting, a difference of 5.25 between spin orbital multiplates and area ratio were maintained ($3d_{5/2}$: $3d_{3/2}$:: 3:2). While we observed the same degree of shift for both Pd $3d_{5/2}$ as well as for Pd $3d_{3/2}$, in the following, we focus on the shift of Pd $3d_{5/2}$ for interpretation. The fitted values of binding energies for different catalysts are presented in table 3.

Catalysts	3d _{5/2} Peak position (Binding energy, eV)	Corresponding %area
Pd/AC	335.60	64.33
T WAL	336.60	35.67
	333.66	11.81
Pd/SiO2	334.74	46.91
1 <i>u/5/0 <u>/</u></i>	336.07	30.88
	337.68	10.40
	333.51	31.42
Pd/Al_2O_3	334.89	49.87
	336.41	18.71
DJ/T:O	333.12	20.63
<i>Fa</i> /110 ₂	334.43	79.37

Table 3: Values of Binding energies for the catalysts (Pd3d_{5/2})



Figure 7: XPS of Pd3d for the catalysts

The Pd $3d_{5/2}$ level binding energy reported for zero valent palladium (Pd⁰) is about 335.2 eV [66–69]. The value obtained for Pd on carbon is about 335.6 eV, which agrees with the value reported by Bertolini et al.[70]. The peak at 336.6 eV is due to PdO_x/Pd[68,69]. In the case of Pd on SiO₂ and Pd on Al₂O₃, we observe peaks showing both positive and negative shifts in the binding energy, while for Pd on TiO₂ only negative shifts were observed. The peaks with the positive shifts are again due to the oxidized forms PdO (336-337.2) and PdO₃ (337.6-337.7)[69].

The binding energy values 334.74 eV and 334.89 eV that we find for Pd on SiO₂ and Al₂O₃, match with those in literature for Pd/SiO_x/Si and Pd/Al₂O₃/Al[71,72]. Sarapatka [72] proposed that interaction between metal and support is by charge transfer at the metal-support interface. Creation of an interface dipole (Pd/Al₂O₃) may attract free electrons from elemental Al to the sample surface. Looking at the differences in electro-negativity of Pd with Si (0.3), Al (0.6) and Ti (0.66), we may surmise the possibility of charge transfer at the metal support interface (support to metal) to be higher for TiO₂ than for Al₂O₃ and SiO₂ (and this would be consistent with the negative shift in the binding energies and their corresponding areas; see Table 3). Bell et al.[67] suggested that negative shifts may be due to SmPd_xO formed during the preparation of catalyst (Sm; Ti, Si, Al). Palladium present in SmPd_xO structure can be more negative than Pd⁰ and cause a negative shift.

Thus the XPS evidence confirms the absence of any significant metal-support interaction in the case of the carbon support, and the existence of varying degrees of interaction in the case of oxide supports, which was suggested by the pulse and TPD results discussed earlier. Electronic interactions, depend on a number of factors such as reducibility of the support, presence of defects, and the nature of support materials[30]. The XPS results are strongly suggestive, in the case of our catalysts, of an interaction involving a shift in the electron cloud towards the metal. In oxidation, this would be expected to lower the capacity of the catalyst to adsorb the hydroxyl species, which is essential for the first step of hydrogen abstraction from the glycerol molecule[9,73]. Metal-support interaction of the kind observed would thus be expected to lower the catalytic activity in the case of glycerol oxidation.

3.5 Acidity and alkalinity of Catalysts

In this work, a CO_2 -pulse has been used to characterize the basic sites of the oxide-supported catalysts. We found that Pd/Al_2O_3 has basic sites, but not Pd/TiO_2 and Pd/SiO_2 .

S.N.	Catalysts	CO ₂ –adsorbed	
		(µmol/g _{catalyst})	
1.	Pd /Al ₂ O ₃	18.6	
2.	Pd /TiO ₂	0.5	
3.	Pd /SiO ₂	1.4	

Table 4: Basicity of the catalyst in terms of CO₂ adsorption capacity

In order to explore the strength and concentration of acidic sites a pyridine-TPD (Fig. 8) was performed. The peaks were de-convoluted by spectra fitting of raw data with Gaussian curve using Fityk0.9.8[74] software. From the Pyridine-TPD (see Figure 8) it is clear that the acidity (per unit weight of catalyst) is more in Pd/Al₂O₃ catalyst, followed by Pd/SiO₂ and then Pd/TiO₂. The desorption peaks (after de-convolution) at temperatures higher than 500^{0} C correspond to strong acid sites[75]. On this basis, the catalysts may be ordered in the decreasing order of acidity as; Pd/Al₂O₃>Pd/TiO₂> Pd/SiO₂. Table 5 reports the results on the basis of catalyst

weight and BET surface area. Pyridine TPD values normalized based on the BET surface area shows that acidic site concentration is more in Pd/TiO₂ than Pd/Al2O3 and Pd/SiO2 but acidic strength follows following trend (based on the desorption temperature peak): Pd/Al2O3>Pd/TiO2>Pd/SiO2.

Table 5: Acidity of the catalysts in terms of area under the curve obtained from pyridine desorption.

Catalysts	Temperature	Peak area/gm of catalyst
	(⁰ C)	(mVs) [×] 10 ⁵
Pd/Al ₂ O ₃	491	0.71
	523	1.32
	603	3.38
Pd/TiO ₂	430	0.052
	497	0.049
	625	0.027
Pd/SiO ₂	358	0.025
	467	0.27
	553	0.017



Figure 8: Pyridine-TPD of oxide supports

In order to further probe the characteristics of the acidic sites (Lewis or Bronsted), FTIR spectroscopy was carried out using pyridine as a probe molecule. No peaks were observed in the region $(1500 - 1540 \text{ cm}^{-1})$ expected for surface-OH groups and coordinated H₂O molecule, which would indicate Bronsted acidic sites[76].All the oxide-supported catalysts used here are thus seen to have predominantly Lewis acid sites.

Pd/AC was not included in these studies because of two reasons. Firstly, the primary motive of the studies was to compare the oxide-supported catalysts, since the supports in these cases does

impart significant acid/base character to the catalyst. Secondly, activated carbons are known to have various oxygenated surface groups such as carboxylic acids, carboxylic anhydrides, lactones, phenols etc, which decompose into CO and CO₂ as the temperature is raised[3,38], and thus cloud any conclusions from studies such as the above.

3.6 Reaction studies

As mentioned in the section on experimental methods, all the reactions were carried out under conditions that ensure the complete absence of internal and external transport limitations. Though the products obtained over all the catalysts studied in this work are same, the activity and selectivity vary significantly. Figure 9 shows the experimental data on glycerol oxidation in the pressurized autoclave. Turnover frequencies (TOF) were calculated based on the initial rates to know the intrinsic activity of the catalysts (mole glycerol converted per sec per mole of metal exposed), and are reported in Table 6. Pd/AC shows a higher activity in comparison to palladium supported on oxide supports investigated, and this is consistent with the type of metal-support interaction inferred on the basis of XPS. The order of activity for different supports is as follows: $Pd/AC>Pd/Al_2O_3>Pd/TiO_2> Pd/SiO_2$. The low activity in the case of silica can also be attributed to the presence of –vely charged [° *Si* – *O*⁻]species on the surface [41], which would make it difficult for the hydroxyl species to adsorb.



Figure 9: Percentage conversion of glycerol with respect to the time

 Table 6: Turnover frequency (TOF) for different catalysts (TOF=moles of glycerol

 reacted/s/mole of exposed palladium dispersed on the catalyst)

Catalysts	TOF (s ⁻¹)
Pd/AC	4.65
Pd/Al ₂ O ₃	1.50
Pd/TiO ₂	0.88
Pd/SiO ₂	0.42

In comparing the activities of catalysts tested in this work with those reported in the literature, we have the difficulty that the catalyst characterization information is often incomplete in the literature, with only metal loading reported and not dispersion. Also, our results above are at an oxygen pressure of 6 bar and a temperature of 60° C, while information from the literature is

available for 3 bar oxygen pressure and 50° C. In order to compare the activity of our catalysts, we carried out experiments at 3 bar oxygen pressure, and correcting these results for the temperature effect based on the activation energy observed in the range $30-60^{\circ}$ C, we obtain a activity of 0.36 s^{-1} (mole glycerol converted per sec *per mole of the metal*) based on initial rates for our most active catalyst (Pd/AC). By way of comparison, Binachi et al.[21] report a figure of 0.32 s^{-1} , Prati et al.[40] report 0.28 s^{-1} , and Dimitratos et al.[22], 0.07 s^{-1} . However, it is possible that the metal dispersion values are quite different between these studies, since the catalysts are prepared by different methods.

The selectivities to the different products are shown as a function of glycerol conversion in Figure 10. For the same level of conversion, significant differences in selectivity to C_3 , C_2 and C_1 products were observed between carbon supported and oxide supported catalysts. For the catalysts studied, the selectivity to glyceric acid is in the same order as the activity. In particular, Pd/AC showed a higher selectivity to C_3 products as compared to oxide-supported palladium, which showed higher levels of formic acid and glycolic acid at similar conversions. We also observed C_2 , C_1 products (Formic and glycolic acids) even at very initial stages of experiments (time t=0), if a nitrogen blanket was not used during the initial heat up. Consideration of carbon balances based on the products analyzed for, showed a shortfall in every case, but the discrepancies were higher in the case of oxide-supported catalysts, indicating a higher incidence of C-C cleavage (leading to a loss of C as CO_2) in the latter cases. These observations suggest that C-C cleavage occurs even at early stages, probably from the intermediate glyceraldehyde. A similar observation has been reported by Ketchie et al.[7]. Following is the trend of carbon balance at higher conversion (i.e., the percentage of glycerol carbon converted that is explained as

by the measured products, values in parenthesis): Pd/AC (72%)> Pd/Al_2O_3 (65%), Pd/TiO_2 (64%)> Pd/SiO_2 (58%). If carbon balance is taken as an indication of the carbon conversion efficiency, then it is seen that the latter is in the same order as activity for the catalysts studied. Figure 10 shows that the selectivity to the primary product glyceric acid for the different catalysts is also in the same order.



Figure 10. Selectivity versus conversion profiles for different catalysts

Since care was taken to eliminate all transport resistances in our experiments, and in view of similarities in metal particle size, differences among the catalysts in terms of their activity and selectivity behavior have to be attributed to the different supports used. Acidity and basicity of the supports and metal-support interaction are the prominent differences among the catalysts.

Recent studies on the mechanism of glycerol oxidation[7,9,13,38,73], highlight the importance of the ability of the catalyst surface to accommodate OH⁻. This depends on the state of palladium and acidic/basic nature of the supports. It has been suggested [7,9,13,73] that, for oxidation in basic solution over gold catalyst, the reaction mechanism involves both solution mediated and metal catalyzed elementary steps. During the catalytic cycle, peroxide formation occurs via reduction of the oxygen before dissociation. Analogous to an electro-catalytic process, the formation and dissociation of peroxide and hydrogen peroxide intermediate occur via a fourelectron or a two-electron transfer process and activation of oxygen occurs through these intermediates. Zope et al.[9] proposed that O₂ played an indirect role by removing electron from the metal surface[9]. These studies show an analogy with CO oxidation in basic solution in terms of electron transfer mechanism, role of hydroxyl, role of O_2 as an electron scavenger (O_2 to O^-) and the role of H₂O₂ during the catalytic cycle. A co-adsorbed hydroxide on the catalyst active surface acts as a Bronsted base to assist in de-protonation[73]. Further the co-adsorbed hydroxide on the catalyst surface can also participate in the C-H activation of the adsorbed alkoxide to produce an adsorbed aldehyde followed by subsequent base-catalyzed formation of gem-diol and dehydrogenation that results in an acid product[9,73].

In case of Pd/AC, palladium is in a higher oxidation state than in oxide supports. The ability to accommodate hydroxide on the Pd/AC is more as compared to the oxide supports. Davis et al.[73] state that the steady-state coverage of hydroxide on the surface is probably limited by the ability of the metal to accommodate the excess negative charge. The higher activity of Pd/AC as compared to Pd/oxide is therefore to be understood in these terms.

While the higher activity/selectivity of the carbon-supported Pd can thus be explained in terms of the lack of any significant support interaction in that case, we need to examine the differences among the oxide-supported catalysts in greater detail. When comparing the activity of the different oxide supports with each other, we did not find any strong correlation with XPS peak shift. However, looking at the acidic-basic properties, which were evaluated by pyridine-TPD and CO₂, a trend exists with respect to the increasing basicity/Acidity. In Table 7, we compare the rates of glycerol conversion by the oxide-supported catalysts on the basis of unit catalyst weight, with the acidities and basicities on the same basis. A good correlation is seen.

Table 7: Comparison the performance of the oxide supported Pd catalysts in relation to their acidity/basicity.

Catalysts	Rate per unit wt of catalyst	Basicity-CO ₂ Adsorbed per unit wt of catalyst	Total Acidity-Pyridine TPD peak area per unit wt of catalyst
	$(mole/g_{cat}.s) \times 10^4$	(µmole/g _{cat})	$(mV.s/g_{cat}) \times 10^5$
Pd/Al ₂ O ₃	1.0105	18.6	5.41
Pd/SiO ₂	0.2696	1.4	0.312
Pd/TiO ₂	0.0705	0.5	0.128

Similar results were observed by Rodrigues et al.[38] for gold supported on different carbon supports. They found that the basic oxygen-free carbon supports were more active, and supports have a secondary role in determining catalytic activity.

 H_2O_2 appears to play a crucial role in determining the selectivity and carbon conversion efficiency via its role in C-C cleavage[7,9,14,15] and this can be considered as one of the reasons for the varying degree of C-C cleavage and higher selectivity to C₁ and C₂ products in case of oxide supported catalysts as compared to Pd/AC. The concentration of H_2O_2 at any point of time would depend on the relative rates of formation and decomposition, In addition to H_2O_2 , the involvement of other factors, such as interaction of reactant and intermediates with the catalyst, also cannot be ruled out in the formation of lower carbon products. These interactions again depend on the acidic/basic characteristics of catalyst, and the defect structures. The supports can play a secondary role, as proposed by Rodrigues et al.[38] for explaining different activities with regards to the different supports for glycerol oxidation reaction catalyzed by gold on the different carbons.

4. Conclusions

Supported palladium catalysts offer significant activity for glycerol oxidation. The activity and product distribution, however, strongly depend on the nature of the support. The present study has shown that the effect of metal-support interaction in glycerol oxidation under alkaline conditions is to reduce both the activity of the catalyst as well as the selectivity to glyceric acid. In general, conditions which favour an adsorption of the [OH⁻] from solution onto the catalyst are likely to lead to high activity and selectivity to glyceric acid, and conditions which promote the

formation of hydrogen peroxide are likely to lead to C-C scission products. In the studies reported here, Pd supported on activated carbon, with the least metal-support interaction, showed the best performance in terms of activity and selectivity as compared to oxide supports. The different characterization methods such as chemisorption, TEM, XPS, TPD etc. employed in this study, clearly indicate varying degrees of metal (Pd)-support interaction, as well as acid/base character among the oxide-supported catalysts. These differences have been seen to be the main reasons for the differences in the performance of the catalysts studied. Electronic interaction between the metal and support is a major factor and we believe that an increase in the electron density around palladium on the oxide support adversely affects the crucial step of the adsorption of hydroxyl species and hence the activity. While further work is needed to understand fully the differences among the oxide-supported catalysts. Further, acidity/basicity is also likely to play an important role in peroxide formation and decomposition that is responsible for C-C cleavage.

Acknowledgements

We acknowledge Department of Science and Technology, New Delhi, India for financing the research grant titled "Studies in catalytic oxidation of glycerol: catalysis, kinetics and reactor engineering". We gratefully acknowledge the support and use of facilities in the SAIF and Central facility, IIT Bombay. AN acknowledge IIT Bombay for TA-Ship and Dr. Sutar (Dept. of Physics, IIT Bombay) for his assistance in exploring the XPS.

References:

- [1] R. Garcia, M. Besson, P. Gallezot, Chemoselective catalytic oxidation of glycerol with air on platinum metals, Appl. Catal. A Gen. 127 (1995) 165–176.
- [2] B. Katryniok, H. Kimura, E. Skrzyńska, J.-S. Girardon, P. Fongarland, M. Capron, et al., Selective catalytic oxidation of glycerol: perspectives for high value chemicals, Green Chem. 13 (2011) 1960–1979. doi:10.1039/c1gc15320j.
- [3] S.E. Davis, M.S. Ide, R.J. Davis, Selective oxidation of alcohols and aldehydes over supported metal nanoparticles, Green Chem. 15 (2013) 17–45. doi:10.1039/C2GC36441G.
- [4] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Selective oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide, Chem. Commun. 7 (2002) 696–697. http://www.ncbi.nlm.nih.gov/pubmed/12119680.
- [5] F. Porta, L. Prati, Selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst: an insight into reaction selectivity, J. Catal. 224 (2004) 397–403. doi:10.1016/j.jcat.2004.03.009.
- [6] S. Demirel, M. Lucas, J. Wärnå, T. Salmi, D. Murzin, P. Claus, Reaction kinetics and modelling of the gold catalysed glycerol oxidation, Top. Catal. 44 (2007) 299–305. doi:10.1007/s11244-007-0303-y.
- [7] W.C. Ketchie, M. Murayama, R.J. Davis, Promotional effect of hydroxyl on the aqueous phase oxidation of carbon monoxide and glycerol over supported Au catalysts, Top. Catal. 44 (2007) 307–317. doi:10.1007/s11244-007-0304-x.
- [8] H. Kimura, K. Tsuto, Selective oxidation of glycerol on a platinum-bismuth catalyst, Appl. Catal. A Gen. 96 (1993) 217–228.
- [9] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, Reactivity of the gold/water interface during selective oxidation catalysis, Science (80-.). 330 (2010) 74–78. doi:10.1126/science.1195055.
- [10] S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nakagawa, K. Tomishige, Performance, structure and mechanism of Pd–Ag alloy catalyst for selective oxidation of glycerol to dihydroxyacetone, J. Catal. 300 (2013) 205–216. doi:10.1016/j.jcat.2013.01.014.

- [11] S. Demirel, M. Lucas, P. Claus, Liquid phase oxidation of glycerol over carbon supported gold catalysts, Catal. Today. 102-103 (2005) 166–172. doi:10.1016/j.cattod.2005.02.033.
- [12] S. Carrettin, P. Mcmorn, P. Johnston, K. Griffin, C.J. Kiely, G.A. Attard, Oxidation of glycerol using supported gold catalysts, Top. Catal. 27 (2004) 131–136.
- [13] W. Ketchie, M. Murayama, R. Davis, Selective oxidation of glycerol over carbonsupported AuPd catalysts, J. Catal. 250 (2007) 264–273. doi:10.1016/j.jcat.2007.06.011.
- [14] W. Ketchie, Y. Fang, M. Wong, M. Murayama, R. Davis, Influence of gold particle size on the aqueous-phase oxidation of carbon monoxide and glycerol, J. Catal. 250 (2007) 94– 101. doi:10.1016/j.jcat.2007.06.001.
- [15] D. Liang, J. Gao, J. Wang, P. Chen, Y. Wei, Z. Hou, Bimetallic Pt—Cu catalysts for glycerol oxidation with oxygen in a base-free aqueous solution, Catal. Commun. 12 (2011) 1059–1062. doi:10.1016/j.catcom.2011.03.019.
- [16] S.D. Pollington, D.I. Enache, P. Landon, S. Meenakshisundaram, N. Dimitratos, A. Wagland, et al., Enhanced selective glycerol oxidation in multiphase structured reactors, Catal. Today. 145 (2009) 169–175. doi:10.1016/j.cattod.2008.04.020.
- [17] D. Liang, J. Gao, H. Sun, P. Chen, Z. Hou, X. Zheng, Selective oxidation of glycerol with oxygen in a base-free aqueous solution over MWNTs supported Pt catalysts, Appl. Catal. B Environ. 106 (2011) 423–432. doi:10.1016/j.apcatb.2011.05.050.
- [18] A. Abbadi, H. Van Bekkum, Selective chemo-catalytic routes for the preparation of βhydroxypyruvic acid, Appl. Catal. A Gen. 148 (1996) 113–122.
- [19] S. Carrettin, P. Mcmorn, P. Johnston, K. Griffin, J. Kiely, G.J. Hutchings, Oxidation of glycerol using supported Pt, Pd and Au catalysts, Phys. Chem. Chem. Phys. 5 (2003) 1329–1336. doi:10.1039/b212047j.
- [20] S. Gil, L. Muñoz, L. Sánchez-Silva, A. Romero, J.L. Valverde, Synthesis and characterization of Au supported on carbonaceous material-based catalysts for the selective oxidation of glycerol, Chem. Eng. J. 172 (2011) 418–429. doi:10.1016/j.cej.2011.05.108.
- [21] C.L. Bianchi, P. Canton, N. Dimitratos, F. Porta, L. Prati, Selective oxidation of glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals, Catal. Today. 102-103 (2005) 203–212. doi:10.1016/j.cattod.2005.02.003.
- [22] N. Dimitratos, J.A. Lopez-sanchez, D. Lennon, F. Porta, L. Prati, A. Villa, Effect of particle size on monometallic and bimetallic (Au, Pd)/C on the liquid phase oxidation of glycerol, Catal. Letters. 108 (2006) 147–153. doi:10.1007/s10562-006-0036-8.

- [23] L. Prati, A. Villa, C. Campione, P. Spontoni, Effect of gold addition on Pt and Pd catalysts in liquid phase oxidations, Top. Catal. 44 (2007) 319–324. doi:10.1007/s11244-007-0305-9.
- [24] N. Dimitratos, A. Villa, L. Prati, Liquid Phase Oxidation of Glycerol Using a Single Phase (Au–Pd) Alloy Supported on Activated Carbon: Effect of Reaction Conditions, Catal. Letters. 133 (2009) 334–340. doi:10.1007/s10562-009-0192-8.
- [25] A. Villa, N. Janjic, P. Spontoni, D. Wang, D.S. Su, L. Prati, Au–Pd/AC as catalysts for alcohol oxidation: Effect of reaction parameters on catalytic activity and selectivity, Appl. Catal. A Gen. 364 (2009) 221–228. doi:10.1016/j.apcata.2009.05.059.
- [26] M. Bowker, P. Stone, P. Morral, R. Smith, R. Bennett, N. Perkins, et al., Model catalyst studies of the strong metal–support interaction: Surface structure identified by STM on Pd nanoparticles on TiO2(110), J. Catal. 234 (2005) 172–181. doi:10.1016/j.jcat.2005.05.024.
- [27] Q. Fu, F.A.N. Yang, X. Bao, Interface-confined oxide nanostructures for catalytic oxidation reactions, Acc. Chem. Res. 46 (2013) 1692–1701.
- [28] E. Gross, G. a. Somorjai, The Impact of Electronic Charge on Catalytic Reactivity and Selectivity of Metal-Oxide Supported Metallic Nanoparticles, Top. Catal. 56 (2013) 1049–1058. doi:10.1007/s11244-013-0069-3.
- [29] G.R. Jenness, J.R. Schmidt, Unraveling the Role of Metal–Support Interactions in Heterogeneous Catalysis: Oxygenate Selectivity in Fischer–Tropsch Synthesis, ACS Catal. 3 (2013) 2881–2890. doi:10.1021/cs4006277.
- [30] G. Pacchioni, Electronic interactions and charge transfers of metal atoms and clusters on oxide surfaces., Phys. Chem. Chem. Phys. 15 (2013) 1737–57. doi:10.1039/c2cp43731g.
- [31] C.T. Campbell, Catalyst-support interactions: Electronic perturbations., Nat. Chem. 4 (2012) 597–8. doi:10.1038/nchem.1412.
- [32] A. Dauscher, R. Touroude, G. Maire, J. Kizling, M. Boutonnet-Kizling, Influence of the Preparation Mode on Metal-Support Interactions in Pt/TiO2 Catalysts, J. Catal. 143 (1993) 155–165.
- [33] M.A. Vannice, R.L. Garten, Metal-Support Effects on the Activity and Selectivity of Ni Catalysts in CO / H2 Synthesis Reactions, J. Catal. 56 (1979) 236–248.
- [34] R. Wojcieszak, M. Zieli, S. Monteverdi, M.M. Bettahar, Study of nickel nanoparticles supported on activated carbon prepared by aqueous hydrazine reduction, J. Colloid Interface Sci. 299 (2006) 238–248. doi:10.1016/j.jcis.2006.01.067.

- [35] S. Demirel, K. Lehnert, M. Lucas, P. Claus, Use of renewables for the production of chemicals: Glycerol oxidation over carbon supported gold catalysts, Appl. Catal. B Environ. 70 (2007) 637–643. doi:10.1016/j.apcatb.2005.11.036.
- [36] I. Sobczak, K. Jagodzinska, M. Ziolek, Glycerol oxidation on gold catalysts supported on group five metal oxides—A comparative study with other metal oxides and carbon based catalysts, Catal. Today. 158 (2010) 121–129. doi:10.1016/j.cattod.2010.04.022.
- [37] A. Villa, A. Gaiassi, I. Rossetti, C.L. Bianchi, K. van Benthem, G.M. Veith, et al., Au on MgAl2O4 spinels: The effect of support surface properties in glycerol oxidation, J. Catal. 275 (2010) 108–116. doi:10.1016/j.jcat.2010.07.022.
- [38] E.G. Rodrigues, M.F.R. Pereira, X. Chen, J.J. Delgado, J.J.M. Órfão, Influence of activated carbon surface chemistry on the activity of Au/AC catalysts in glycerol oxidation, J. Catal. 281 (2011) 119–127. doi:10.1016/j.jcat.2011.04.008.
- [39] P. Gallezot, Selective oxidation with air on metal catalysts, Catal. Today. 37 (1997) 405–418.
- [40] L. Prati, A. Villa, F. Porta, D. Wang, D. Su, Single-phase gold/palladium catalyst: The nature of synergistic effect, Catal. Today. 122 (2007) 386–390. doi:10.1016/j.cattod.2006.11.003.
- [41] Y. Niibori, M. Kunita, O. Tochiyama, T. Chida, Dissolution Rates of Amorphous Silica in Highly Alkaline Solution, J. Nucl. Sci. Technol. 37 (2000) 349–357. doi:10.1080/18811248.2000.9714905.
- [42] S.J. Tauster, Strong metal-support interactions, Acc. Chem. Res. 20 (1987) 389–394. doi:10.1021/ar00143a001.
- [43] S.J. Tauster, S.C. Fung, R.L. Garten, Strong Metal-Support Interactions . Group 8 Noble Metals Supported on TiO2, J. Am. Chem. Soc. 100(1) (1978) 170–175.
- [44] R. Burch, A.R. Flambard, Metal-Support Interactions in Nicke/Titania Catalysts: The Importance of Interfacial Phenomena, J. Catal. 78 (1982) 389–405.
- [45] R.T.K. Baker, E.B. Prestridge, G.B. McVicker, The Interaction of Palladium with Alumina and Titanium Oxide Supports, J. Catal. 89 (1984) 422–432.
- [46] M.L. Toebes, J.A. Van Dillen, K.P. De Jong, Synthesis of supported palladium catalysts, J. Mol. Catal. A Chem. 173 (2001) 75–98.
- [47] S. Oyama, X. Zhang, J. Lu, Y. Gu, T. Fujitani, Epoxidation of propylene with H2 and O2 in the explosive regime in a packed-bed catalytic membrane reactor, J. Catal. 257 (2008)

1-4. doi:10.1016/j.jcat.2008.04.023.

- [48] M.A. Smith, M.G. Ilasi, A. Zoelle, A Novel Approach To Calibrate Mesopore Size from Nitrogen Adsorption Using X-ray Diffraction: An SBA-15 Case Study, J. Phys. Chem. C. 117 (2013) 17493–17502. doi:10.1021/jp400284f.
- [49] P. Mcmorn, G. Roberts, G.J. Hutchings, Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts, Catal. Letters. 63 (1999) 193–197.
- [50] P. Weerachawanasak, P. Praserthdam, M. Arai, J. Panpranot, A comparative study of strong metal–support interaction and catalytic behavior of Pd catalysts supported on micron- and nano-sized TiO2 in liquid-phase selective hydrogenation of phenylacetylene, J. Mol. Catal. A Chem. 279 (2008) 133–139. doi:10.1016/j.molcata.2007.10.006.
- [51] M.A. Vannice, S.-Y. Wang, S.H. Moon, The Effect of SMSI (Strong Metal-Support interaction) Behavior on CO Adsorption and Hydrogenation on Catalysts, J. Catal. 166 (1981) 152–166.
- [52] H. Dropsch, M. Baerns, CO adsorption on supported Pd catalysts studied by adsorption microcalorimetry and temperature programmed desorption, Appl. Catal. A Gen. 158 (1997) 163–183.
- [53] E. V Benvenutti, L. Franken, C.C. Moro, FTIR Study of Hydrogen and Carbon Monoxide Adsorption on Pt/TiO2, Pt/ZrO2, and Pt/Al2O3, Langmuir. 15 (1999) 8140–8146.
- [54] W.-J. Shen, M. Okumura, Y. Matsumura, M. Haruta, The influence of the support on the activity and selectivity of Pd in CO hydrogenation, Appl. Catal. A Gen. 213 (2001) 225– 232. doi:10.1016/S0926-860X(01)00465-3.
- [55] S. Ladas, H. Poppa, M. Boudart, The Adsorption and catalytic oxidation of carbon monoxide on evaporated palladium particles, Surf. Sci. 102 (1981) 151–171.
- [56] S.N. Pavlova, V.A. Sadykov, V.A. Razdobarov, E.A. Paukshtis, The Influence of Support on the Low-Temperature Activity of Pd in the Reaction of CO Oxidation, J. Catal. 161 (1996) 507–516.
- [57] S. Rieck, A.T. Bell, The Influence of Dispersion on the Interactions Pd / SiO2 of H2 and CO with Pd/SiO2, J. Catal. 54 (1987) 46–54.
- [58] W.C. Conner Jr., J.L. Falconer, Spillover in Heterogeneous Catalysis, Chem. Rev. 95 (1995) 759–788. doi:10.1021/cr00035a014.
- [59] M.L. Cubeiro, J.L.G. Fierro, Partial oxidation of methanol over supported palladium catalysts, Appl. Catal. A Gen. 168 (1998) 307–322. doi:10.1016/S0926-860X(97)00361-

Х.

- [60] N. Iwasa, S. Kudo, H. Takahashi, S. Masuda, N. Takezawa, Highly selective supported Pd catalysts for steam reforming of methanol, Catal. Letters. 19 (1993) 211–216. doi:10.1007/BF00771756.
- [61] C.-T. Hong, C.-T. Yeh, F.-H. Yu, Effect of Reduction and Oxidation Treatments on Pd/ZnO Catalysts, Appl. Catal. 48 (1989) 385–396. doi:10.1016/S0166-9834(00)82807-9.
- [62] E. Rocchini, M. Vicario, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, Reduction and Oxygen Storage Behavior of Noble Metals Supported on Silica-Doped Ceria, J. Catal. 211 (2002) 407–421. doi:10.1006/jcat.2002.3719.
- [63] C.-T. Hong, C.-T. Yeh, F.-H. Yu, Effect of Reduction and Oxidation Treatments on Pd/ZnO Catalysts, Appl. Catal. 48 (1989) 385–396. doi:10.1016/S0166-9834(00)82807-9.
- [64] M. Jin, J.-N. Park, J.K. Shon, J.H. Kim, Z. Li, Y.-K. Park, et al., Low temperature CO oxidation over Pd catalysts supported on highly ordered mesoporous metal oxides, Catal. Today. 185 (2012) 183–190. doi:10.1016/j.cattod.2011.09.019.
- [65] R.W.M. Kwok, XPS Peak Fitting Program for WIN95/98 XPSPEAK version 4.1, (2000) XPS Peak Fitting Program for WIN95/98 XPSPEAK 4.1.
- [66] B.L. Mojet, J.T. Miller, D.E. Ramaker, D.C. Koningsberger, A New Model Describing the Metal – Support Interaction in Noble Metal Catalysts, J. Catal. 186 (1999) 373–386.
- [67] T. Bell, H. Fleisch, An XPS Study of Metal-Support Interactions on Pd/SiO2 and Pd/La2O3, J. Catal. 413 (1984) 398–413.
- [68] K. Noack, Z. Heinz, Identification of the State of Palladium in Various Hydrogenation Catalysts by XPS, Catal. Letters. 4 (1990) 145–155.
- [69] NIST X-ray Photoelectron Spectroscopy (XPS) Database, Version 3.5, NIST X-Ray Photoelectron Spectrosc. Database, Version 3.5. (2014). http://srdata.nist.gov/xps/.
- [70] J.C. Bertolini, P. Delichere, B.C. Khanra, J. Massardier, C. Noupa, B. Tardy, Electronic properties of supported pd aggregates in relation with their reactivity for 1,3-Butadiene hydrogenation, Catal. Letters. 6 (1990) 215–224.
- [71] B. Schleich, D. Schmeisser, W. Gopel, Structure and reactivity of the system Si/SiO2/Pd: A combined XPS, UPS and HREELS study, Surf. Sci. 191 (1987) 367–384.
- [72] T.J. Sarapatka, Pd-Induced Charge Transports with Pd/Al2O3/Al Interface Formation, J. Phys. Chem. (1993) 11274–11277.

- [73] M.S. Ide, R.J. Davis, The Important Role of Hydroxyl on Oxidation Catalysis by Gold Nanoparticles., Acc. Chem. Res. 47 (2013) 825–833. doi:10.1021/ar4001907.
- [74] M. Wojdyr, Fityk: A general-purpose peak fitting program, J. Appl. Crystallogr. 43 (2010) 1126–1128. doi:10.1107/S0021889810030499.
- [75] J.R. Copeland, I.A. Santillan, S.M. Schimming, J.L. Ewbank, C. Sievers, Surface Interactions of Glycerol with Acidic and Basic Metal Oxides, J. Phys. Chem. C. 117 (2013) 21413–21425. doi:10.1021/jp4078695.
- [76] M.I. Zaki, M.A. Hasan, F.A. Al-Sagheer, L. Pasupulety, In situ FTIR spectra of pyridine adsorbed on SiO2–Al2O3, TiO2, ZrO2 and CeO2: general considerations for the identification of acid sites on surfaces of finely divided metal oxides, Colloids Surfaces A Physicochem. Eng. Asp. 190 (2001) 261–274. doi:10.1016/S0927-7757(01)00690-2.