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Effect of Structure and Substituents in the Aqueous Phase Oxidation of Alcohols and Polyols Over Au, Pd, and Au–Pd Catalysts

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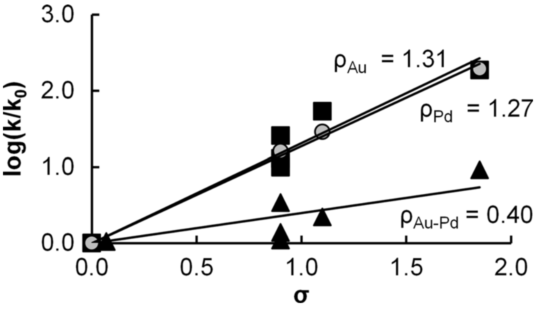
Abstract Reactivity trends for oxidation of various alcohols and polyols have been examined for carbon-supported Au, Pd, and Au–Pd catalysts. A Hammett *σρ* approach was used to study substituent effects, with Hammett factors (*ρ*) of 1.27, 1.31, and 0.40 obtained for Pd, Au, and Au–Pd catalysts, suggesting the formation of a net negative charge at the transition state of the rate limiting step. The lower *ρ* for the Au–Pd catalyst versus Au and Pd monometallic catalysts indicates the ability of the Au–Pd catalyst to stabilize the negative charge at the transition state, explaining the improved performance of Au–Pd bimetallic catalysts for alcohol oxidation. Hammett–Taft factors were used to explain the low selectivity of terminal diols and polyols to diacids.

Graphical Abstract



Keywords Alcohol oxidation · Aqueous phase · Diacids · Hammett equation · Hammett–Taft factors

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1 Introduction

Much effort has been expended on the study of alcohol and polyol oxidation over carbon-supported Au and Au-containing catalysts. These reactions are often conducted in strongly basic aqueous media. There remain many issues concerning activity trends of Au versus Au–Pd bimetallic compositions and role of O_2 in the reaction mechanism [1–3]. Other issues that remain unanswered include (1), why is typically only the monoacid product observed for the selective oxidation of glycerol. Diacids are rarely observed for any catalyst system; this is especially important since tartronic acid represents a higher value chemical intermediate than glyceric acid and (2), why are the oxidation rates of alcohols so different? Oxidation rates of n-propanol are much lower than those of either 1,2-propanediol or 1,3-propanediol, which are in turn less reactive than glycerol over the same catalysts at the same reaction conditions and pH values [2–4].

The role of added OH^- on activity has also been studied, and, for supported Au catalysts, the rate of glycerol oxidation is negligible when an excess of OH^- relative to glycerol is not used. Likewise, for supported Pd and Pt catalysts and Au–Pd bimetallic catalysts, the activities for glycerol oxidation are much higher at high pH values [2, 5–7]. As literature reports have stated [4, 6, 8], the first step in alcohol oxidation reactions is abstraction of a H atom from a terminal –OH to form an alkoxy species. This can either occur in the liquid phase by the action of free OH^-, as in the case for supported Au catalysts, or by both free OH^- and adsorbed alcohol to form an adsorbed alkoxy species, as is presumably the case for Pd, Pt, or Au–Pd catalysts, since Group VIII metals are active for dehydrogenation of alcohols. However, the activities for Pt and Pd catalysts are greatly enhanced when excess OH^- is present [2, 5–7].

Thus, the acid dissociation constants (K_a) for alcohols should be considered when examining reactivity trends for alcohols and polyols.

In this communication, we discuss the reactivity trends for various alcohols and diols over carbon-supported Au, Pd, and Au–Pd catalysts and relate activities to the different K_a values. Correlations of K_a values with Hammett and Taft inductance factors are also made and used to offer an explanation for the low rates of formation of diacids from the oxidation of glycerol.

2 Experimental Section

2.1 Materials

Glycerol, ethylene glycol, and 3-chloro-1-propanol were purchased from Sigma Aldrich. 1,2-propanediol, 1,3-propanediol, and 1-propanol were purchased from Alfa Aesar. The 5 wt% Pd/CP-97 carbon catalyst (supplied by BASF Catalysts Inc.) consisted of 4.4 nm Pd particles (24 % Pd dispersion). The same CP-97 carbon was also used to make the supported Au catalyst. Sodium hydroxide (NaOH) pellets (BDH) were used to provide OH^- in the reaction media. Sodium carbonate (Na_2CO_3), gold chloride (Na $AuCl_4 \cdot 3H_2O$) (Alfa-Aesar), and formaldehyde (HCHO, 37 %) (Sigma Aldrich) were used for preparation of the supported Au catalyst. A Thermo Scientific Barnstead Nanopure system supplied 18.2 MΩ-cm de-ionized water that was used for all applications.

2.2 Catalyst Preparation and Characterization

Preparation procedures for the 1 % Au/C and the Au–Pd/C bimetallic catalyst have been reported in previously published work [4, 8]. For the 1 % Au/C catalyst, solution of $HAuCl_4$ 0.1 M (1 ml) was diluted with distilled water (10 ml) and was added to a stirred slurry of carbon (2 g) in distilled water (20 ml). A saturated solution of Na_2CO_3 was added until a fixed pH of 10 was reached. The slurry was allowed to stand for 1 h, then heated to 70 °C and reduced by dropwise addition of 1.5 ml of HCHO (37 %). Preparation of the Au–Pd/C bimetallic catalyst by electroless deposition has also been described previously [8, 9]. The bimetallic catalyst has been characterized previously by using H_2 titration of oxygen pre-covered Pd sites and X-ray diffraction measurements [8], showing 0.46 Au coverage on Pd at an overall composition of 1.1 wt% Au and 4.9 wt% Pd. The 5 % Pd/C catalyst has been characterized previously by using H_2 titration of oxygen pre-covered Pd sites, while the 1 % Au/C catalyst has been characterized X-ray diffraction measurements [8].

2.3 Oxidation Reactions

The aqueous phase oxidation of the different compounds was performed in a 100 ml EZE-Seal™ batch reactor (Autoclave Engineers), using the same protocol as our previously published work [4, 8]. The impeller turbine used for these experiments (Dispersimax™, Autoclave Engineers) has a hollow shaft with holes that are positioned both above the liquid level and between the individual turbine blades within the liquid. As a result, O_2 mixing was very efficient in the liquid reaction medium. The O_2 gas pressure above the liquid level is considerably higher than in the liquid vortex at the impeller turbine which provides excellent radial and axial mixing of O_2 in the liquid to minimize mass transfer effects of O_2 in the aqueous reaction medium, as opposed to a stirrer with solid shaft.

The reaction conditions used in this study were similar to those that have been reported by others for alcohol oxidation [2–4, 8, 10], specifically $T = 60$ °C, $P(O_2) = 145$ psig, 80 ml of 0.10 M solution of reactant alcohol, and 1.0 M NaOH concentration.

3 Results and Discussion

Oxidation reactions for eight different substrates were carried out over three different catalysts; 5 wt% Pd/C, 1 wt% Au/C and the bimetallic Au–Pd/C catalyst (~0.5 coverage of Au on Pd). Table 1 shows reaction rate constants for the different substrates over the different catalysts, normalized to the amount of catalyst used. The substrate alcohols are arranged in order of decreasing activities for the Au–Pd/C catalysts. Rate constant calculated from a first order fit of reaction data.

Table 1 First order reaction rate constants for oxidation of different substrates on Pd, Au, and Au–Pd catalysts

Substrate	Rate constants 1/[(g cat)*h]		
	Pd/C	Au/C	0.46 Au–Pd/C
Glycerol	1.59	1.86	34.31
1,6-Hexanediol	0.00	0.10	12.71
1,2-Propanediol	0.24	0.54	8.28
Ethylene glycol	0.13	0.13	5.17
1,3-Propanediol	0.00	0.26	4.11
3-Chloro,1-propanol	–	–	3.91
1-Propanol	0.01	0.00	3.75

Rate constants have been normalized to the amount of catalyst used (1/h divided by mass of catalyst). Reaction conditions: $T = 60$ °C, $P(O_2) = 145$ psig, 80 ml of 0.10 M solution of reactant alcohol, and 1.0 M NaOH concentration, catalyst mass of 0.150 g for Pd/C, 0.300 g for Au/C, and 0.060 g for 0.46 Au–Pd/C

3.1 Effect of K_a on Reaction Rate

As has been previously reported [2, 4, 11], the first step in the oxidation of alcohols in aqueous, basic media is the abstraction of a proton from the hydroxyl group. Most evidence points to this step occurring in solution between free OH^- and the alcohol, rather than adsorbed on the catalyst surface [1, 5, 11]. Using the Henderson–Hasselbalch equation (Eq. 1), the concentration of the deprotonated species can be calculated for each alcohol under the reaction conditions.

$$pH = pK_a - \frac{[A^-]}{[HA]} \tag{1}$$

Table 2 shows the concentration of the protonated and deprotonated species at zero reaction time (pH 14), as well as the percent of the substrate present as the deprotonated species in solution. Comparison of reaction rate constants in Table 1 with the initial concentrations of deprotonated alcohols (A^-) in Table 2 indicates there is a strong correlation between reactivity and the extent of deprotonation, or more specifically, the dissociation constant (K_a). This correlation holds true for all three catalysts, even though Pd, in particular, can form alkoxides by both deprotonation in solution and adsorbed alcohols to form adsorbed alkoxy species. In order to better understand this relationship, a closer look at the kinetics of the rate limiting step is necessary.

Previous work has shown that oxidation of alcohols does not proceed in the absence of a base when using Au catalysts, and is greatly inhibited when using Pd catalysts [1, 5, 6, 11]. Most evidence points to the initial deprotonation of a terminal –OH group of the substrate being a solution-phase phenomenon driven by free hydroxyl ions [1, 2, 4, 6, 8, 11]. The equilibrium reaction for the deprotonation of the alcohol is written as:

$$RCH_2OHRCH_2O^- + H^+ \tag{2}$$

Table 2 Acid dissociation constants for different substrates, concentration of protonated and deprotonated species, and extent of deprotonation at pH 14 and t = 0

Substrate	pK_a	$[A^-]$ (mol/l)[a]	$[HA]$ (mol/l)[a]	%$[HA] \rightarrow [A^-]$
Glycerol	14.15	0.041	0.059	41.5
1,6-Hexanediol	15.10	0.007	0.093	7.40
1,2-Propanediol	14.90	0.011	0.089	11.2
Ethylene glycol	15.10	0.007	0.093	7.40
1,3-Propanediol	15.10	0.007	0.093	7.40
3-Chloro,1-propanol	15.93	0.001	0.099	1.20
1-Propanol	16.00	0.001	0.099	1.00

[a] Initial substrate concentration of 0.1 M

For this reaction, the equilibrium constant, or K_a, the acid dissociation constant, can be stated as:

$$K_a = \frac{[RCH_2O^-][H^+]}{[RCH_2OH]} \tag{3}$$

Rearranging the self-ionization constant for water (Eq. 4) and inserting it into Eq. 3 gives the dissociation constant (Eq. 5).

$$K_w = [OH^-][H^+] \Rightarrow [H^+] = \frac{K_w}{[OH^-]} \tag{4}$$

$$K_a = \frac{[RCH_2O^-]K_w}{[RCH_2OH][OH^-]} \tag{5}$$

Equation 5 can then be solved for the concentration of the deprotonated species,

$$[RCH_2O^-] = \frac{K_a}{K_w}[RCH_2OH][OH^-] \tag{6}$$

In previous work [4] we showed the existence of a kinetic isotope effect for the oxidation of d_4-ethylene glycol ($HOCD_2CD_2OH$) over both Au/C and bimetallic Au–Pd/C catalysts, indicating that C–H bond scission was the rate-limiting step. If we assume the same step is rate determining for all terminal alcohols, the rate expression can be written as:

$$RCH_2O^- + 2^* \xrightarrow{k_1} RCHO^* + H^* \tag{7}$$

$$r_{RCHO} = k_1[RCH_2O^-] \tag{8}$$

where * represents a catalytically active site. Equation 8 is consistent with our results and the correlation of reaction rates with the extent of deprotonation reported in Table 2.

Finally, Eq. 8 can be rewritten using Eq. 6 to give:

$$r_{RCHO} = k_1\frac{K_a}{K_w}[RCH_2OH][OH^-], \tag{9}$$

where the direct dependence of the rate of the RDS on the concentration of the substrate alcohol, OH^- concentration, and magnitude of K_a are readily apparent. The first order dependency of alcohol conversion on RCH_2OH is also consistent with the first order decay plots of glycerol, ethylene glycol, and 1,2-propanediol observed in our previous work [4, 8].

3.2 Hammett Correlations

In order to determine how substrate structure is related to the activity trends, the Hammett equation (Eq. 10) [12] was used to compare 1-propanol to other substrates. The substrate alcohols in this study can be viewed as substituted propanols.

$$log\left(\frac{k}{k_0}\right) = \sigma\rho \tag{10}$$

Table 3 pK_a and σ values for the series of substrates

Substrate	pK_a	σ ($pK_{a(H)} - pK_a$)
Glycerol	14.15	1.85
Ethylene glycol	15.10	0.90
1,2-Propanediol	14.90	1.10
1,3-Propanediol	15.10	0.90
1,6-Hexanediol	15.10	0.90
3-Chloro,1-propanol	15.93	0.07
1-Propanol	16.00	0.0

Values taken from [17]

The parameters of Eq. 10 are: k_0, the reaction rate constant for propanol conversion; k, the reaction rate constant for each of the substituted alcohols; σ, the substituent constant; and ρ, the reaction constant. The substituent constant σ is defined as the difference of the pK_a of the unsubstituted compound ($pK_{a(H)}$, propanol in the present case) and the pK_a of the substituted compound (Table 3) [12–14]. Table 3 shows the pK_a and σ values for the series of alcohols in this study. Propanol has a pK_a of 16.00, while all other substrates have lower pK_a values. This results in positive σ values for all the different substituted compounds. Aliphatic, linear compounds are expected to exhibit only inductive effects and not the resonance effects observed for substituted aromatic structures [12]. This means the substituents will have a net electron withdrawing effect, consistent with tabulated values for Hammett σ values for –OH and –Cl groups tabulated in the literature [12, 15, 16].

Figure 1 shows the Hammett plots for the oxidation of the series of substrates over the Au/C, Pd/C and Au–Pd/C catalysts. Hammett reaction constant ρ are all positive values, indicating the development of a negative charge at the reaction center in the transition state of the rate limiting step [12, 13, 18]. The difference in value of the reaction constants ρ helps explain the difference in the catalytic behavior of the three catalysts. Both Au and Pd have similar values of ρ and rather similar rates of reaction (Table 1) for the different alcohols, suggesting similar negative charge distributions at the transition state. The Au–Pd catalyst, on the other hand, is approximately 20 times more active than either Au or Pd, while the reaction constant ρ (0.40) is much smaller than for either Au or Pd (1.31 and 1.27, respectively).

As we have previously reported [8], the fact that the maximum in activity occurs at a Au coverage of 0.5 on the Pd surface suggests a bifunctional effect where both Pd and Au sites are involved in the rate determining step. For non-site specific deposition of Au on Pd, the maximum, statistical concentration of bimetallic Au–Pd site pairs occurs at a coverage of 0.5. Previous work from our group [19] has, in fact, shown that Au is deposited in a uniform manner over all Pd surface sites using the same ED bath, consistent with the above hypothesis. The lower catalytic activity at lower Au coverages is due to a smaller number of these types of bifunctional sites (the activity is more similar to Pd) and at higher coverages the extra Au atoms produce larger domains of Au and even three-dimensional Au structures, which lowers the numbers of Pd–Au site pairs to give catalyst performance resembling pure Au surfaces.

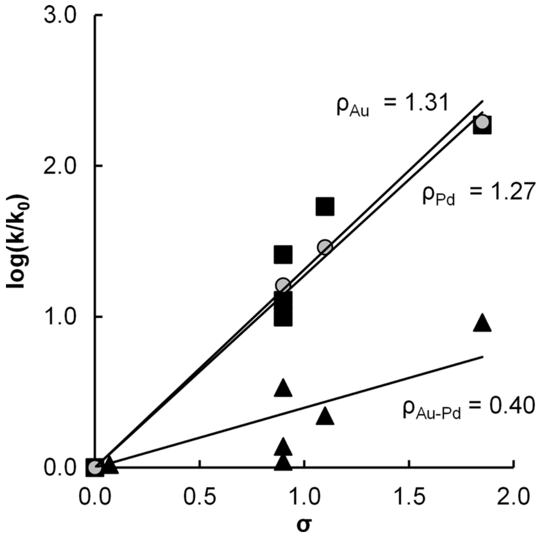

Fig. 1 Hammett plots for the alcohols from Table 3 over carbon-supported Au, Pd, and Au–Pd catalysts

XPS data for the series of catalysts with coverage from 0 to 1.0 [4, 8] showed that BE shifts for the Au 4f region did not correlate with the trend in activity (shifts to lower BE values were larger in magnitude at lower coverages), suggesting that electronic effects are not responsible for the increased activity of the Au–Pd catalysts. Furthermore, a similar family of Ag–Pd/C catalysts was prepared and studied to determine whether geometric/ensemble effects were responsible for the enhanced activity of particular Au–Pd compositions, since Ag should be as effective as Au for formation of Pd ensembles. However, there was no bimetallic effect for the Ag–Pd catalysts, suggesting that ensemble effects were not responsible for the improved activity of the 0.5 Au–Pd/C catalyst. Thus, the enhanced activity of intermediate coverages of Au on the Pd surface is due to the formation of bifunctional Au–Pd sites and the fact that activity is a maximum suggests the bifunctional site is a Au–Pd site pair.

The new insight provided by the Hammett Correlations provides an explanation of the nature of the interaction of reaction intermediates with the bimetallic site. The Au–Pd site stabilizes the charge of the transition state by distributing the negative charge between Pd and Au sites to give a nominal, five-membered ring transition state at the

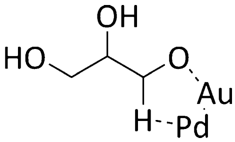

Fig. 2 Stabilization of glycerol reaction intermediate at transition state

rate-limiting step (C–H bond breaking shown in Fig. 2). We propose that the electron-rich Au site interacts more weakly with the C–O bond (Au···O–C), permitting facile desorption of products, while the active Pd site interacts more strongly with the C–H bond, which increases the rate of dehydrogenation of α Carbon. For the monometallic catalyst, the Pd interaction would be more centered on the C–H bond (Pd is an excellent hydrogenation–dehydrogenation catalyst), while Au interacts primarily with the C–O bond, since it forms C–O bonds much more easily than C–H bonds [8]. Gold is also a poor dehydrogenation catalyst which would make C–H bond breaking more difficult. This is consistent with DFT results published by Medlin et al. [4], who report a decrease in the barrier for C–H scission for the Au–Pd bimetallic catalyst compared to monometallic Au, and also a decrease in coverage of strongly bound adsorbates compared to monometallic Pd catalysts.

3.3 Positive σ and its Effect on Selectivity

Previous results for alcohol oxidation have shown that while Au, Pd, and Au–Pd catalysts are highly selective for the formation of carboxylic acids, selectivity to the corresponding dicarboxylic acids are usually very low or nonexistent [4, 11, 20–22]. For glycerol, the most selective secondary product is usually glycolic acid formed via C–C bond cleavage, while terminal diols typically form only the monocarboxylic acid [4, 10].

Given the accepted mechanism for alcohol oxidation, formation of a dicarboxylic acid likely proceeds through sequential oxidation, first to a carboxylic acid and then to the dicarboxylic acid [6, 22]. The pK_a of the second dissociation constant for a diol must be higher than the first one, meaning that the σ value will be lower than that of the diol. This in turn results in a low reaction rate for oxidation of the second –OH group (or the remaining –OH group of the monocarboxylic acid).

To better understand the effects of substituents on pK_a values, it is more useful to use Taft factors, rather than Hammett factors, since Taft factors are more relevant to aliphatic systems where only inductive effects are present [15, 16]. For Taft factors, substituent effects fall off with increasing distance from the reaction center by a factor of 0.36 for every $–CH_2–$ group. The positive Taft factor of 1.34 for the –OH group, indicative of an electron withdrawing effect can also be used to explain the difference in pK_a values for 1-propanol, 1,2-propanediol and 1,3-propanediol in Table 2. The e^--withdrawing effect of the –OH group on the C_2 of 1,2-propanediol increases the acidity of the neighboring $–CH_2OH$ group, which makes formation of $–CH_2O^- + H^+$ easier and lowers the pK_a value to 14.9, compared to 16.00 for 1-propanol. For 1,3-propanediol, the inter-positioning of the $–CH_2–$ group lowers the e^--withdrawing effect of the –OH group at the C_3 position, which then increases the pK_a to 15.10.

Application of the same reasoning to the effect of the terminal carboxylate group of the glycerate anion ($HOCH2CHOHCOO^-$) from oxidation of glycerol helps to understand the low rates of formation of tartronic acid (or 1,3-diglycerate dianion in basic media). The Taft factor for the –COO– is −1.06 [15], indicating it is strongly e^--releasing. This lowers the acidity of the O–H group at the C3 position; the –COO– group inhibits the ability to deprotonate the remaining terminal –OH group.

A second factor inhibiting the formation of a dicarboxylic acid is the consumption of base during reaction. Davis [22] determined the consumption of OH^- during glycerol oxidation over an Au/TiO_2 catalyst to be 1.92 mol of hydroxyl ions consumed per mole of glycerol reacted. The rate expression in Eq. 9 shows alcohol oxidation is directly related to OH^-, thus the deprotonation of the second, terminal –OH group would be hindered to effectively suppress the sequential oxidation pathway. Davis [22] showed that for the same catalyst the oxidation rate of glyceric acid to tartronic acid increased for higher $[OH^-]$/[glyceric acid] ratios. Even so, TOF values for conversion of glyceric acid were much lower than for glycerol conversion; at an OH^- concentration of 0.6 M the TOF for glyceric acid conversion was 0.1 s^{-1}, compared to 4.9 s^{-1} for glycerol, and only increased to 0.47 s^{-1} when OH^- concentration was increased to 2.0 M. This is consistent with the proposed effect of –COO– to limit the ability to deprotonate the second –OH group and the resulting reaction inhibition.

The results for oxidation of glycerol over the 0.460 Au–Pd/C bimetallic catalyst in this study are shown in Fig. 3. At longer reaction times (>1.5 h) there is a slow decrease in the selectivity to glyceric acid from 74 to 68 % at 5 h of reaction; conversely, the selectivity to tartronic acid increased from 5 to 10 % over the same time period. Glycolic acid (11 %) and oxalic acid (2 %), both of which are C2 monoacid and diacid, respectively, were also observed, but are not discussed since the C–C cleavage necessary to form these products is an additional complication and not the intent of this study. This slow formation of tartronic acid is consistent with the proposed effect of OH^- concentration and pK_a on reaction rate and selectivity. These results in this study are similar to those reported by Davis [22] for oxidation of glycerol using 1.6 % Au/TiO_2 in a batch reactor. Glycerol conversion

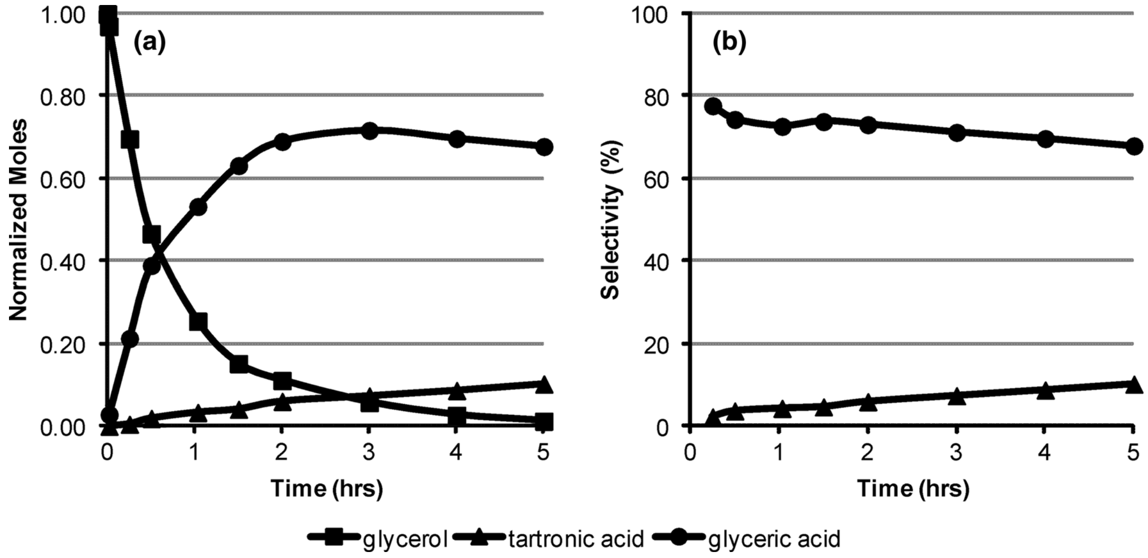

Fig. 3 **a** Normalized moles versus reaction time and **b** selectivity for monoacid (glyceric acid, *circles*) and diacid (tartronic acid, *triangles*) for glycerol (*squares*) oxidation over 0.46 Au–Pd/C catalyst

was carried out for 12 h to observe the formation of diacids. Selectivity to glyceric acid was 63 at 33 % conversion, and increased to 69 at 85 % conversion, while selectivity to tartronic acid was 2 and 4 %, respectively. The conversion to diacids was very slow and the overall selectivity to tartronic acid and oxalic acid remained <10 % even after 12 h of total reaction time. On the other hand Prati [23] evaluated gold supported on a commercial, basic anion resin for the oxidation of glycerol in a batch reactor and observed relatively high selectivity to tartronic acid; at 90 % glycerol conversion the selectivities to glyceric acid and tartronic acid were 49 % and 16 %, respectively. However, increasing the $[OH^-]/[glycerol]$ ratio from 1:1 to 4:1 resulted in a decrease of tartronic acid, with 60 % selectivity to glyceric acid and only 8 % to tartronic acid. Turnover frequency for glycerol conversion increased by a factor of four, but the lower selectivity to tartronic acid is inconsistent with other published results and the consecutive pathway for tartronic acid formation.

The present batch reactor results suggest two possibilities to overcome low selectivity to dicarboxylic acid products. The first is to simply increase the OH^- concentration of the solution [6]. This is not practical, due to the already high concentrations that currently make these reactions unattractive. Further, the logarithmic nature of the pH scale means that very high concentrations of OH^- would be required. The second option is to tailor a catalyst that reacts with the –OH groups of these substrates to form adsorbed RO^- species. Such an intermediate could react to form an aldehyde and then the acid, eliminating the need for the hydroxide catalyzed deprotonation in solution.

4 Conclusions

Oxidation of a family of alcohols, diols, and polyols has been studied to diagnose reactivity trends of different substrates. The Hammett $\sigma\rho$ approach was used to study the dependence of substrate structure with reactivity. The linear dependency between σ and the logarithm of the reaction rates (relative to n-propanol) gave different positive slopes ρ for the reactions of the different alcohols for the three catalysts studied. This implies that a negative charge is developed at the reaction center during the rate-limiting step, and that electron withdrawing groups promote activity. The low selectivity of terminal diols and polyols to form dicarboxylic acids (or dicarboxylate anions in basic media) by the sequential oxidation of the second terminal –OH group of the monocarboxylate anion is likely due to the combination of two factors. The first is the low reactivity of the second –OH group caused by the inhibiting effect of the $-COO^-$ group at the other terminus; the second factor is the necessarily high pK_a of the second –OH groups and the lower concentration of OH^- remaining after formation of the monocarboxylate species. The kinetic expression for the oxidation of the different alcohols reveals the direct dependence of the rate-limiting step to the K_a of the substrate and the concentration of deprotonated substrate in solution.

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