On the deactivation of supported platinum catalysts for selective oxidation of alcohols

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The oxidation of a variety of terminal alcohols with O₂ in liquid water at 343 K over Pt supported on C, BN, SiO₂, TiO₂, and Al₂O₃ was explored to determine the origin of catalyst deactivation. The sintering of Pt nanoparticles and dissolution of Pt did not contribute significantly to the observed deactivation. A decrease in TOF for 1,6-hexanediol oxidation after the exposure of Pt/C to dioxygen was easily reversed by reduction with the alcohol substrate, indicating that over-oxidation of Pt was not the mode of deactivation. Strongly adsorbed CO on Pt was observed by ATR-IR spectroscopy after contacting the catalysts with alcohols, but the CO was easily removed by oxidation with dissolved O₂. Results from thermogravimetric analysis and regeneration studies indicate a strongly adsorbed species other than CO and product acid deactivated the catalysts.

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1. Introduction

The production of high-value chemicals from biomass is a promising strategy to economically convert bio-renewable carbohydrates. The selective oxidation of alcohols derived from biomass feedstocks is a particularly attractive route when the oxidation can be performed in an environmentally friendly manner [1]. The selective oxidation of alcohols to acids in water over heterogeneous catalysts with molecular oxygen as the oxidant is a green chemistry alternative to traditional petrochemical oxidation reactions with toxic, inorganic oxidants [2]. Two prominent examples of green oxidation reactions are the conversion of glycerol to glyceric acid, a valuable additive for cosmetics, and the transformation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, a monomer for bio-renewable plastics [3,4].

One of the major challenges of alcohol oxidation catalysis by supported metals is deactivation. The deactivation of Pt catalysts during alcohol oxidation [5] and electro-oxidation [6] has been suggested to be a major barrier to commercialization. Although common modes of catalyst deactivation such as metal particle sintering or metal leaching might contribute to observed behavior, a frequent explanation for platinum deactivation during alcohol oxidation is the formation of an inactive oxide surface layer produced by the over-oxidation of the Pt catalyst [7–12]. Indeed, irreversible deactivation of Pt is speculated by some to be caused by oxygen atoms that penetrate the Pt lattice and form sub-oxides that are not easily reduced by the alcohol substrate [13–16]. In contrast, there is some evidence that Pt is fairly resistant to oxidation by dioxygen in the presence of water [17]. Another explanation of Pt deactivation during alcohol oxidation is the strong adsorption of byproducts produced during the reaction [18]. For example, base-catalyzed aldol condensation reactions of products formed in alkaline solution yield species capable of strongly adsorbing to the Pt surface [19–21]. Furthermore, during the electro-oxidation of 1,2-ethanediol and methyl-a-D-glucopyranoside over Pt in basic electrolyte solution, CO was observed by infrared (IR) spectroscopy to be adsorbed to the Pt surface [22]. Similar evidence for the formation of adsorbed CO during electro-oxidation of 1,3-propanediol, benzyl alcohol, and glycerol has been reported [23–25]. The poisoning of Pt electrodes by CO during the electro-oxidation of alcohols has been recognized for more than two decades. In addition to CO, IR spectroscopy also revealed evidence of strongly adsorbed hydrocarbon species (CₓHᵧ) formed during the electro-oxidation of glycerol on the Pt surface [26].

Recent studies of glycerol oxidation in aqueous solution over Pt/C have reported the formation of CO₂ at acidic conditions and moderate temperature (373 K) [27,28]. The oxidation of CO derived from the C–C bond breaking of glycerol on Pt was suggested as the origin of CO₂. In situ ATR-IR spectroscopy identified CO as an adsorbed species during the anaerobic dehydrogenation of benzyl alcohol in cyclohexane on Pd/Al₂O₃ [29,30]. The adsorbed CO was
produced via benzaldehyde decarbonylation and blocked further benzyl alcohol dehydrogenation. Adsorbed CO was also identified by ATR-IR spectroscopy during the liquid-phase anaerobic dehydrogenation of benzyl alcohol over Pt/Al2O3 in toluene at 323 K [31]. The role of surface adsorbates on Pt during aqueous alcohol oxidation and what effect, if any, they have in the deactivation of supported Pt is particularly intriguing.

The goal of this work is to explore the various modes of deactivation of supported platinum catalysts used for alcohol oxidation reactions to elucidate the appropriate strategies for improving catalyst stability. The dissolution of Pt metal, sintering of Pt nanoparticles, over-oxidation of the Pt surface, and poisoning by strongly adsorbed products formed in solution or on the Pt surface were all investigated. Although we studied the oxidation of both mono- alcohol and diol substrates, most of our experiments focused on the oxidation of 1,6-hexanediol because of its potential importance in the production of bio-renewable adipic acid [32].

2. Materials and methods

2.1. Catalyst preparation

The 2.69 wt% Pt/C and the 4.86% Pt/Al2O3 were obtained from Aldrich Chemical Co. The Pt/C catalyst was reduced in 100 cm3·min−1 of flowing H2 for 4 h at 473 K, cooled, exposed to air, and stored at ambient temperature. The SiO2 (Sigma–Aldrich) supported Pt (2 wt%) and TiO2 (Degussa P25) supported Pt (3 wt%) were prepared by incipient wetness impregnation of aqueous chloroplatinic acid (Sigma–Aldrich). The 2% Pt/SiO2 and 3% Pt/TiO2 catalysts were dried in air for 12 h at 393 K followed by calcination in 100 cm3·min−1 of flowing air for 4 h at 673 K. The catalysts were then reduced in 100 cm3·min−1 of flowing H2 for 4 h at 673 K, cooled, exposed to air, and stored at ambient temperature. A boron nitride (Aldrich) supported Pt (5 wt%) catalyst was prepared in a similar manner to the oxide supported catalysts, except the 5% Pt/BN was not calcined prior to reduction in H2 for 4 h at only 473 K.

2.2. Catalyst characterization

The metal dispersion of the Pt catalysts was determined by H2 chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. The supported Pt catalysts were heated to 473 K at 4 K·min−1 under flowing H2 (GT&S 99.999%) and reduced for 2 h. The samples were then evacuated and held for 2 h at 473 K before being cooled to 308 K for analysis in the pressure range of 10–450 Torr. The amount of surface metal available for catalysis was evaluated by the total amount of H2 adsorbed, extrapolated to zero pressure, assuming a stoichiometry (H2/PTsurf) equal to unity.

Elemental analysis (using ICP–AES performed by Galbraith Laboratories, 2323 Sycamore Drive, Knoxville, TN 37921) determined a Pt loading of 2.69 wt% for the Pt/C catalyst and 4.86 wt% for the Pt/Al2O3 catalyst. The leaching of Pt into solution was measured by elemental analysis of the filtrate after 24 h of 1,6-hexanediol oxidation for Pt/C and Pt/Al2O3.

To prepare the fresh and used 2.69% Pt/C sample for transmission electron microscopy (TEM), ~1 mg of sample was suspended in 2 cm3 of ethanol by agitating the mixture for 30 min in a sonication bath. A copper grid with a carbon film was briefly dipped in the solution and the ethanol was then evaporated. The imaging of the catalyst was performed on a FEI Titan operating at 180 kV and equipped with a Gatan 794 Multi-scan Camera (EFTEM). The used Pt/C sample for TEM was recovered from the reactor (see below) after 24 h of 1,6-hexanediol oxidation at 343 K.

2.3. Alcohol oxidation

The semi-batch aqueous alcohol oxidation reactions were performed in a 50 cm3 Parr Instrument Company 4592 batch reactor with a 30 cm3 glass liner. The appropriate amounts of substrate, acetic acid (to lower the pH), and catalyst were added to approximately 10 cm3 of distilled, deionized water in the glass liner. The importance of eliminating artifacts from mass transfer resistances and using added organic acid during the evaluation of alcohol oxidation kinetics over Pt has been discussed in detail in previous work [32]. The glass liner was inserted into the reactor, sealed, purged with He, and heated to 343 K. The reaction was initiated by pressurizing the reactor with 10 bar absolute O2 (GT&S, 99.993%). The pressure was maintained at a constant value by continuously feeding O2. No conversion was observed after 240 min when N2 was substituted for O2.

Product samples were periodically removed from the reactor and the catalyst was filtered using 0.2 µm PTFE filters before analysis with a Waters e2695 high pressure liquid chromatograph (HPLC). The HPLC was equipped with refractive index and UV/Vis detectors. Product separation in the HPLC was carried out with an Aminex HPX-87H column (Bio-Rad) operating at 318 K with 5 mM H2SO4 in water flowing at 5 cm3·min−1. The retention times and calibration curves were determined by injecting known concentrations of standards. The initial turnover frequency (TOF) [mol alcohol converted (mol Pt/surf)−1·s−1] for alcohol oxidation was calculated from the initial conversion of the alcohol, usually within the first 15 min of the reaction. Selectivity to a specific product is defined as moles of that product formed divided by moles of all products produced. For the recycle experiments, the catalyst was recovered from solution by centrifugation at 400 RPM for 30 min. The catalyst was then washed with DI water and subsequently recovered ten times to remove loose surface contaminants before re-use in oxidation experiments.

Thermogravimetric analysis (TGA) was performed with a SDT Q600 (TA Instruments). A constant heating rate of 10 K·min−1 from room temperature to 973 K with a He or H2 purge flow of 50 ml·min−1 was used for all experiments. The amount of sample loaded in the TGA was approximately 20 mg. The used Pt/BN was recovered from solution by centrifugation after 24 h of ethanol oxidation at 343 K and 10 bar O2 in a similar manner to the recycle experiments. Before the TGA experiments, both the fresh and used Pt/BN were dried overnight in air at 393 K.

The evaluation of headspace gas was performed after batchwise aqueous alcohol oxidation at 343 K and 3 bar of dioxygen. After 20 h, the gas in the headspace volume was analyzed by a gas chromatograph (HP 5890 Series II) equipped with a thermal conductivity detector (TCD) for detection and quantification of CO2, CO, and CH4 with known response factors [33]. Gas separation was carried out with a ShinCarbon ST 80/100 packed column. The pressure of the headspace did not change significantly during the reaction. When a blank experiment with just the Pt/C catalyst was performed (no alcohol substrate), a small amount of CO2 was observed. This background amount of CO2 was subtracted from all other experiments that used Pt/C as the catalyst. The oxidation of ethylene glycol (EG) without a catalyst produced negligible amounts of CO2.

2.4. In situ ATR-IR spectroscopy

The in situ ATR (attenuated total reflectance) IR spectra were collected on a Bruker Vertex 70 spectrometer with a liquid nitrogen cooled MCT detector. The spectra were recorded by co-adding 300 scans at 4 cm−1 resolution from approximately 4000 to 700 cm−1. Background spectra were collected with N2, H2, or O2 saturated distilled, deionized water flowing at 1 cm3·min−1 over
the coated internal reflectance element (IRE) at 5 bar and 298 K. In a typical procedure, the Pt/SiO₂ or Pt/BN catalyst was deposited onto a cylindrical ZnSe IRE (8.255 cm × 0.635 cm) by dipping the IRE in a well-dispersed aqueous solution of 1 wt% catalyst followed by drying at 393 K. The procedure was repeated ten times or until a thin layer of catalyst covered the surface of the IRE. The IRE was then secured in a stainless steel continuous flow reactor cell mounted on an ATR attachment (Axiom Analytical TNL-130). The Pt/SiO₂ and Pt/BN catalyst layers were tested for stability up to 10 bar.

The N₂, O₂, or H₂ saturated water solutions and N₂ or O₂ saturated alcohol solutions were prepared by flowing 100 cm³ min⁻¹ of gas at atmospheric pressure through the solution in a stainless steel reservoir for 1 h. The alcohol solution was either 0.1 M benzyl alcohol or ethanol saturated with the desired gas at ambient pressure. After the solution was purged with gas at atmospheric pressure, the pressure in the reservoir was increased to 5 bar and the solution was switched to a N₂ or O₂ saturated alcohol solution for approximately 60 min prior to subsequently purging the cell with flowing N₂ saturated H₂O to remove the alcohol substrate from the cell. In some cases, O₂ or H₂ saturated H₂O was pumped to the cell.

3. Results and discussion

3.1. Catalyst characterization

The Pt weight loading and H₂ chemisorption results of the carbon, boron nitride and oxide supported Pt catalysts are provided in Table 1. The 2.69% Pt/C catalyst has been extensively characterized in other work [32]. The fraction of platinum exposed, also referred to as dispersion (d), was determined by hydrogen chemisorption for all of the catalysts. The Pt/C, Pt/SiO₂, and Pt/TiO₂ catalysts had a similar platinum dispersion (0.57–0.65) and thus a similar estimated particle size (1/d) of about 2 nm. The Pt/Al₂O₃ sample had a lower dispersion compared to the other oxide supported catalysts. The Pt/BN catalyst also had a low dispersion (0.1), despite the lower reduction temperature of 473 K compared to 673 K for the oxide supported catalysts. The low surface area (24 m² g⁻¹) of boron nitride and the absence of surface functional groups to anchor platinum may have contributed to the low dispersion [34].

Fig. 1(a) shows a TEM image of the fresh Pt/C sample revealing an average diameter of 1.7 nm ± 1.2 nm, which is consistent with results from H₂ chemisorption.

3.2. Deactivation of Pt during alcohol oxidation

Fig. 2 depicts reaction profiles of various alcohols oxidized over Pt/C in liquid water at 343 K. In particular, the influence of acetic acid on the profile of 1,6-hexanediol oxidation is directly compared. The rate of conversion of 1,6-hexanediol decreased significantly after about 1 h regardless of the presence of acetic acid. The inhibition of the initial rate of 1,6-hexanediol oxidation over Pt/C by organic acids was explored in other work [32]. While the initial rate of 1,6-hexanediol oxidation was a little greater (0.27 s⁻¹) without acetic acid compared to when acetic acid was present (0.19 s⁻¹), the reaction profile was similar and the conversion of 1,6-hexanediol after 4 h was approximately the same. Thus, regardless of whether organic acid was present at the start of the reaction or produced in situ by the oxidation of 1,6-hexanediol to 6-hydroxyhexanoic acid, the Pt/C catalyst deactivated in a similar manner. An increase in the concentration of acetic acid from 0.35 M to 0.7 M at the start of the reaction neither changed the initial rate of 1,6-hexanediol oxidation nor the reaction profile of oxidation (not shown). It should be noted that under the conditions of this study, the order of reaction with respect to 1,6-hexanediol is zero, suggesting the decrease in rate with time as illustrated in Fig. 2 is the result of catalyst deactivation [32].

The oxidation of ethanol and 1,3-propanediol over Pt/C in the presence of acetic acid also produced reaction profiles consistent with significant catalyst deactivation during the first hour of oxidation (Fig. 2). Ethanol and 1,6-hexanediol had initial rates of oxidation that were approximately four times faster than that of 1,2-ethanediol and 1,3-propanediol [32], yet the Pt/C catalyst deactivated in each case. Interestingly, the oxidation of 1,2-ethanediol showed just a minor decrease in oxidation activity up to 2 h.

![Fig. 1. Comparison of (a) fresh and (b) deactivated 2.69% Pt/C catalyst with bright field TEM images.](image-url)
but the rate slowed considerably after that. The reaction profile of benzyl alcohol oxidation over Pt/C did not reveal significant deactivation as compared to all of the other substrates investigated at these conditions, but severe Pt deactivation during benzyl alcohol oxidation has been reported [35].

Fig. 3 displays the reaction profiles for 1,6-hexanediol over Pt/C, Pt/BN, Pt/Al₂O₃, Pt/TiO₂, and Pt/SiO₂. Regardless of the support for the Pt nanoparticles, a decrease in the initial rate of oxidation was observed after about 1 h. The low TOF observed over Pt/SiO₂ and Pt/TiO₂ compared to all of the other samples (Table 2) was unexpected and we do not yet have an explanation for this phenomenon. Nevertheless, the deactivation of Pt during 1,6-hexanediol oxidation as consistent across the entire range of support and Pt particle sizes used in this study.

### 3.3. Pt leaching and sintering

The irreversible deactivation of a supported Pt catalyst during alcohol oxidation by physical modification of the surface through leaching or sintering could significantly decrease catalyst activity.

### Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (s⁻¹)</th>
<th>Conv. (%)</th>
<th>Liquid Sel. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.69% Pt/C</td>
<td>0.19</td>
<td>20</td>
<td>94</td>
</tr>
<tr>
<td>5% Pt/BN</td>
<td>0.20</td>
<td>22</td>
<td>96</td>
</tr>
<tr>
<td>2% Pt/SiO₂</td>
<td>0.04</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>3% Pt/TiO₂</td>
<td>0.06</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>4.86% Pt/Al₂O₃</td>
<td>0.24</td>
<td>14</td>
<td>100</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 M 1,6-hexanediol, 1,6-hexanediol:Pt = 500:1 (mol:mol), T = 343 K, pO₂ = 10 bar, 0.35 M acetic acid, pH = 2.5, ALD = 6-hydroxyhexanal and HA = 6-hydroxyhexanoic acid.

The leaching of platinum into aqueous solution at low pH is mentioned frequently as a possible cause of deactivation in the electro-oxidation literature [36]. To determine the extent of platinum leaching from the 2.69% Pt/C catalyst, elemental analysis of the filtrate was performed after 24 h of 1,6-hexanediol oxidation. Table 3 shows that 1.5% of the total amount of Pt loaded in the reactor leached into solution. When an identical experiment was performed with 4.86% Pt/Al₂O₃, approximately 0.82% of the total available Pt and 2.9% of the total Al leached into solution. The dissolution of the alumina support by corrosion or leaching at acidic conditions may have contributed to the presence of Pt in solution. In an effort to probe the potential reactivity of soluble Pt, a hot filtration experiment was performed in aqueous acetic acid. The Pt/C catalyst was removed from the reactor after 1 h of 1,6-hexanediol oxidation that reached 32% conversion. The conversion of the diol substrate in the filtrate remained unchanged at 32% after an additional hour at reaction conditions. The concentration of product aldehyde was also stable in the reaction medium after the removal of the catalyst, confirming the lack of measurable activity associated with soluble Pt.

The presence of carboxylic acids in solution has been associated with the promotion of Pt leaching from the catalytic surface [37]. During the oxidation of 1,6-hexanediol, the pH of solution decreased from 6.5 to 2.5 as 100% conversion of 1,6-hexanediol produced an 85% yield of adipic acid. The ratio of adipic acid to leached Pt was approximately 6,400, however, despite a pKₐ of 4.43, the organic acid did not appear to cause considerable leaching of Pt. In the literature, a small amount of Pt was reported to leach into solution even at basic conditions. Prati et al. determined that a 5% Pt/C catalyst leached approximately 2% of the total platinum metal available after four 2 h recycle experiments involving glycerol oxidation at 323 K and a pH of 13 [38]. After the oxidation of 5-hydroxymethylfurfural at 373 K and a pH of 8, approximately 2–3% of the available platinum had leached from a 5.1% Pt/C catalyst after 12 h [39]. The oxidation of methyl-α-β-glucopyranoside over Pt/C had a 4% loss of platinum after five 8 h recycle experiments at 323 K and a pH of 9 [40]. The leaching of small amounts of Pt into the aqueous solution after 24 h of alcohol oxidation is not ideal for industrial application; however, the low level of Pt leaching does not appear to contribute significantly to the extensive deactivation of the catalyst observed after just 4 h.

The sintering of metal nanoparticles can occur by metal atom migration across the support or by metal dissolution followed by re-deposition onto other metal nanoparticles (Ostwald ripening). Either process would increase the average particle size of the catalyst. The severe sintering of graphite-supported Pt at 363 K in aqueous solution in a hydrogen atmosphere has been reported in the literature [40]. Thus, the Pt particle size of the Pt/C catalyst was evaluated by TEM (Fig. 1) before and after the oxidation of 1,6-hexanediol for 24 h at 343 K and acidic aqueous conditions. Table 1 shows that the Pt particle size slightly increased from 1.7 nm for the fresh catalyst to 1.9 nm for the used catalyst. The
increase in Pt metal particle size is relatively small compared to the severe decrease in alcohol oxidation rate after 24 h.

Despite the numerous reports of Pt deactivation during aqueous alcohol oxidation, sintering has been infrequently investigated in the literature. After the oxidation of methyl-α-D-glucopyranoside over Pt/C at 323 K for 2.8 h at basic conditions (pH = 9), a small increase in particle size from 1.45 nm to 1.64 nm was observed by TEM, whereas the dispersion measured by the chemisorption of CO decreased from 0.56 for the fresh Pt/C to 0.27 for the used Pt/C [40]. The chemisorption protocol included a reduction with dihydrogen at 373 K. The catalyst deactivation in that work was hypothesized to be the influence of a strongly adsorbed species.

3.4. Effect of startup conditions and recycle experiments

To explore the possibility of Pt over-oxidation as a cause of catalyst deactivation, Pt/C was exposed to several different startup conditions before the oxidation of 1,6-hexanediol. Table 4 shows the TOF determined for 1,6-hexanediol oxidation at 343 K and 10 bar O2 at acidic conditions. In a typical experiment, the Pt/C catalyst was heated to 343 K in the presence of 1,6-hexanediol in an inert (He) atmosphere for 0.5 h. During this inert treatment, Pt is reduced by the alcohol from a slightly oxidized state (from exposure to air) to metallic, which is considered the active site for alcohol dehydrogenation [7]. The inert startup conditions gave an initial TOF for 1,6-hexanediol oxidation of 0.19 s⁻¹. When the Pt/C catalyst was exposed to flowing O2 in water for 2 h at 343 K (oxidative treatment) and 1,6-hexanediol was added to initiate the reaction, the TOF decreased by 79% to 0.04 s⁻¹. However, the exposure of the oxidized Pt/C catalyst to 1,6-hexanediol in an inert atmosphere for just 0.5 h (inert treatment) recovered a significant portion of the catalytic activity (0.15 s⁻¹) and a 1 h inert treatment after purposefully exposing the Pt to O2 recovered almost all of the catalytic activity for 1,6-hexanediol oxidation (0.17 s⁻¹). While the initial oxidation activity of Pt did decrease after the O2 treatment, the surface oxygen was apparently easily removed by reduction of the catalytic surface with an alcohol. These results are analogous to experiments in the literature that demonstrate how a Pt catalyst can be partially regenerated in a flow reactor by flowing N2 instead of air in the presence of methyl-α-D-glucopyranoside for a short period of time [15]. In addition, evidence from X-ray absorption spectroscopy suggests that the presence of water inhibits platinum oxide formation [41,42].

Given the fact that over-oxidation of the Pt was easily reversed by an inert gas treatment in alcohol, a deactivated Pt/C sample was recovered by centrifugation after 4h of 1,6-hexanediol oxidation at 343 K and subsequently washed ten times. The recovered catalyst was then subjected to an inert gas treatment in alcohol for 1 h. The initial 1,6-hexanediol oxidation activity of the washed and recycled catalyst (0.04 s⁻¹) was measured to be 79% less than that of the fresh catalyst. Thus, a significant portion of the original Pt/C activity was not recovered by the alcohol substrate treatment and most likely could not be attributed to over-oxidation of the Pt surface (Table 4). When the recovered and washed Pt/C catalyst was treated with either flowing He or H2 at 473 K without water, a significant increase in 1,6-hexanediol oxidation activity was observed. While the He treatment was mildly effective at recovering the catalytic activity of Pt with a TOF of 0.12 s⁻¹, the H2 treatment regenerated most, but not all, of the initial oxidation activity with a TOF of 0.17 s⁻¹ (Table 4). The regeneration of Pt/C by a high-temperature H2 treatment after methyl-α-D-glucopyranoside oxidation was also shown to be effective [15]. Although the reduction of Pt by alcohol substrate in water was not effective at regenerating catalytic activity, a high-temperature H2 treatment was, which suggests a strongly adsorbed but reducible species on Pt may be one cause of deactivation.

To give more insight into why the H2 treatment was more effective than the He treatment, a thermogravimetric analysis of the fresh and used (after 24 h of ethanol oxidation in the batch reactor) Pt/BN catalyst was performed. The Pt/BN catalyst was used because of boron nitride’s relatively stable and inert character as a support compared to carbon or the oxide supports. The inertness of boron nitride is valuable because it contains less functionalized groups on the surface, which may decrease the strong adsorption of products or byproducts. The Pt/BN catalyst was recovered from solution by centrifugation and then washed and subsequently recovered ten times to remove loose surface contaminants. The catalyst was then dried overnight at 393 K before being loaded onto the TGA sample platform.

Fig. 4 shows the weight loss profile of the fresh (no prior reaction) and the used Pt/BN catalyst in 50 cm³ min⁻¹ of He with a ramp rate of 10 K min⁻¹. A small weight loss was observed for the fresh and used catalyst at temperatures lower than 423 K and was attributed to desorption of weakly adsorbed water or carbon dioxide from the air. The used Pt/BN sample clearly showed a relatively large weight loss between 523 K and 643 K. The overall weight loss of 0.32% for the used Pt/BN sample was double that of the fresh catalyst at 0.15%, but the actual weight losses were very small compared to the total mass of the catalyst. The TGA results of the used Pt/BN catalyst explain why the treatment in He at 473 K was only able to partially restore activity (Table 4). The regeneration treatment likely removed some strongly adsorbed species, but was not at a sufficiently high temperature to completely remove all species from the Pt surface. When the used Pt/BN catalyst was instead exposed to H2, the sample lost mass (0.34% after 12 h) prior to the temperature ramp (not shown). Upon the start of the temperature ramp, the sample showed an additional loss in mass for a total overall loss of 0.43%. Thus, the adsorbed species was more easily removed from the catalyst surface in H2 compared to He. These results are consistent with those in Table 4 that show the regeneration of oxidation activity upon exposure to H2 at 473 K was more efficient than that in He.

### Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Adipic acid yield (%)</th>
<th>Pt leached (%)</th>
<th>Adipic acid:Leached Pt (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.69% Pt/C</td>
<td>85</td>
<td>1.5</td>
<td>6400</td>
</tr>
<tr>
<td>4.86% Pt/Al2O3</td>
<td>91</td>
<td>0.82</td>
<td>8900</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 M 1,6-hexanediol, 1,6-hexanediol:Pt = 100:1 (mol:mol), T = 343 K, pO2 = 10 bar, 24 h.

### Table 4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TOF (s⁻¹)</th>
<th>% Decrease in oxidation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert (0.5 h)</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Oxidative (2 h)</td>
<td>0.04</td>
<td>79</td>
</tr>
<tr>
<td>Oxidative (2 h) then Inert (0.5 h)</td>
<td>0.15</td>
<td>71</td>
</tr>
<tr>
<td>Oxidative (2 h) then Inert (1 h)</td>
<td>0.17</td>
<td>71</td>
</tr>
<tr>
<td>Recycle then Inert (1 h)</td>
<td>0.04</td>
<td>79</td>
</tr>
<tr>
<td>Recycle then H2 at 473 K (2 h) then Inert (0.5 h)</td>
<td>0.12</td>
<td>71</td>
</tr>
<tr>
<td>Recycle then H2 at 473 K (2 h) then Inert (0.5 h)</td>
<td>0.17</td>
<td>11</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 M 1,6-hexanediol, 1,6-hexanediol:Pt = 500:1 (mol:mol), T = 343 K, pO2 = 10 bar, 0.35 M acetic acid. Inert treatment: N2 with aqueous 1,6-hexanediol. Oxidative treatment: flow O2 in water. Recycle: catalyst recovered after 4h of 1,6-hexanediol oxidation and washed with DI water. H2 and He treatment under flowing gas.
3.5. Influence of chemical additives

Given the results from leaching studies, electron microscopy, and thermogravimetric analysis, the inhibition of supported Pt catalysts by strongly adsorbed byproducts of alcohol oxidation was suspected to partially account for deactivation. Since the number of catalytic sites is typically very low compared to the amount of substrate molecules, only trace quantities of strongly adsorbing species could deactivate the catalyst. Some researchers suggest that carboxylic acids, the primary product of alcohol oxidation under aqueous conditions, can strongly adsorb on Pt, so the inhibition of 1,6-hexanediol oxidation by carboxylic acids and the effect of concentration was recently investigated [32]. As discussed earlier, a moderate decrease in the initial oxidation rate of 1,6-hexanediol (30%) was observed upon the addition of 0.35 M acetic acid, but the deactivation behavior was similar (Fig. 2). Therefore, we explored the influence of a variety of additives on the oxidation reaction in the presence of excess acetic acid and the results are summarized in Table 5. Addition of adipic acid did not affect the rate of 1,6-hexanediol oxidation, suggesting the diacid product is not the inhibitory agent responsible for deactivation. The addition of 6-hydroxyhexanoic acid decreased the initial TOF of 1,6-hexanediol oxidation by 42%, but this result was most likely the result of competitive oxidation rather than inhibition.

Mallet et al. suggested that Pt/C deactivated because of strong adsorption of aldol dimerization products of the substrate 1-methoxy-2-propanol at basic conditions with NaOH [19]. Bonello et al. proposed that aldol condensation of methyl pyruvate poisoned the Pt surface even in the absence of oxygen [20,21]. Similarly, Zope et al. determined that at basic conditions, compounds with secondary alcohol groups could be oxidized to ketones that would form products that strongly adsorb on the surfaces of Au and Pt catalysts [4]. Table 5 presents the effect of adding secondary alcohols and ketones on the initial rate of 1,6-hexanediol oxidation over Pt. The addition of 0.1 M acetone had no effect on the alcohol oxidation rate. This is consistent with reports in the literature that low concentrations (<0.4 M) of acetone had no effect on the oxidation rate of 2-propanol over Pt/SiO2 at neutral conditions [43]. As shown in Table 5, addition of the secondary alcohols 2,4-pentanediol and 2,3-butanediol did not affect the rate of oxidation. In contrast, the addition of 2,4-pentanedione and of mesityl oxide resulted in an 84% and 68% decrease in oxidation activity, respectively. Apparently, under the acidic conditions of this study, secondary alcohols and mono-ketones (acetone) do not strongly adsorb on the Pt surface during alcohol oxidation. The low pH prevents the rapid formation of aldol condensation products that can

Table 5

<table>
<thead>
<tr>
<th>Additive</th>
<th>Structure</th>
<th>TOF (s⁻¹)</th>
<th>% Decrease in oxidation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>6-Hydroxyhexanoic acid</td>
<td></td>
<td>0.11</td>
<td>42</td>
</tr>
<tr>
<td>Adipic acid</td>
<td></td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>2,4-Pentanediol</td>
<td></td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td></td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>2,4-Pentanedione</td>
<td></td>
<td>0.03</td>
<td>84</td>
</tr>
<tr>
<td>Mesityl oxide</td>
<td></td>
<td>0.06</td>
<td>68</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 M 1,6-hexanediol, 1,6-hexanediol:Pt = 500:1 (mol/mol), T = 343 K, pO2 = 10 bar, 0.35 M acetic acid, pH = 2.5, 0.1 M additive.
block metal sites. In contrast, addition of aldol products or diketones substantially lowers the rate of alcohol oxidation, presumably by strong adsorption on Pt.

3.6. Detection of byproducts

Table 6 shows the amount of CO₂ produced in the headspace of the reactor after alcohol oxidation for 20 h at 343 K and 3 bar O₂. As mentioned in the Introduction, CO has been observed in both the electro-catalytic and heterogeneous catalytic oxidation of alcohols over Pt. The production of CO₂ during glycerol oxidation has been observed over Pt at acidic aqueous conditions [27,28]. Evaluation of headspace was performed to gain insight into the byproducts of selective alcohol oxidation reactions. The production of CO₂ was observed during oxidation of mono-alcohols, diols, and benzyl alcohol. While the quantification of small amounts of CO₂ was difficult, the overall carbon balance based on the moles of carbon in the identified products (Table 6) was adequate for qualitative comparisons.

The amount of CO₂ produced from 1,2-ethanediol and 1,3-propanediol was significantly higher than from ethanol or 1,6-hexanediol. When the amount of catalyst loaded in the reactor was doubled to achieve a high conversion of 1,3-propanediol, both 1,3-propanediol and 1,2-ethanediol produced similar amounts of CO₂. Interestingly, the initial rate of oxidation was faster for ethanol and 1,6-hexanediol than for 1,2-ethanediol and 1,3-propanediol (Fig. 2). The addition of acetic acid to solution did not change the amount of CO₂ produced during 1,6-hexanediol oxidation and acetic acid did not undergo a significant amount of oxidative decarboxylation at these reaction conditions. One potential route for the production of CO₂ is the decarboxylation of diacids produced during diol oxidation. For example, malonic acid is known to decarboxylate without a catalyst at higher temperatures [44]. While both malonic acid and adipic acid produced some CO₂ in the presence of O₂ and Pt/C, the conversion of the diacid was much slower than the conversion of the corresponding diol, and the diacid produced less CO₂ than the diol over the same period of time. Interestingly, the oxidative decarboxylation of malonic

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conv. (%)</th>
<th>CO₂ Prod. (mol × 10⁻⁴)</th>
<th>CB Liq. Prod. (%)</th>
<th>CB Gas Prod. (%)</th>
<th>Total CB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Pt/C)</td>
<td>-</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Ethanediol (No Pt/C)</td>
<td>0</td>
<td>0.043</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Ethanediol</td>
<td>94</td>
<td>6.3</td>
<td>74.1</td>
<td>29.9</td>
<td>104.0</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>38</td>
<td>1.0</td>
<td>89.4</td>
<td>8.5</td>
<td>97.9</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>84</td>
<td>5.0</td>
<td>86.2</td>
<td>18.9</td>
<td>105.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>91</td>
<td>0.41</td>
<td>99.7</td>
<td>2.1</td>
<td>101.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>95</td>
<td>0.33</td>
<td>97.7</td>
<td>1.8</td>
<td>99.5</td>
</tr>
<tr>
<td>1,6-Hexanediol</td>
<td>71</td>
<td>0.79</td>
<td>92.5</td>
<td>1.9</td>
<td>94.3</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0</td>
<td>0.081</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HDO + Acetic Acid</td>
<td>78</td>
<td>0.77</td>
<td>90.9</td>
<td>1.6</td>
<td>92.5</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>3</td>
<td>0.92</td>
<td>68.7</td>
<td>52.7</td>
<td>121.4</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>3</td>
<td>0.28</td>
<td>82.5</td>
<td>15.4</td>
<td>97.9</td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>98</td>
<td>0.68</td>
<td>97.8</td>
<td>1.0</td>
<td>98.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction conditions: 0.1 M Substrate, Sub.:Pt = 500:1 (mol:mol), T = 343 K, pO₂ = 3 bar, 20 h. Carbon balance (CB) (%) = [(mol carbon in products)/(mol carbon substrate converted)] × 100.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Background CO₂ production from Pt/C alone subtracted from other experiments.</td>
</tr>
<tr>
<td>b Substrate to Pt ratio = 250:1 (mol:mol).</td>
</tr>
<tr>
<td>c Methane production measured to be 0.063 mol × 10⁻⁴ or 3900 ppm at 3 bar and 343 K.</td>
</tr>
<tr>
<td>d After headspace analysis, 3 bar H₂ injected for 1 h. Methane and ethane observed.</td>
</tr>
<tr>
<td>e Experiment performed with 2% Pt/SiO₂.</td>
</tr>
</tbody>
</table>

![Fig. 5. In situ ATR-IR spectra of aqueous benzyl alcohol (a) saturated with N₂ flowing over Pt/SiO₂ and the production of CO adsorbed on Pt (b) over 20 min at 5 bar and 298 K. The water background has been removed.](image-url)
acid produced almost a quantitative amount of acetic acid, while no acetic acid was observed in either of the 1,3-propanediol experiments (no initial amount of acetic acid was added in either experiment). Thus, decarboxylation of the product acid was not considered the primary route of CO₂ production.

The decarbonylation of an aldehyde to CO that subsequently can be oxidized to produce CO₂ is another possible reaction path. Mondelli et al. observed adsorbed CO during ATR-IR spectroscopy of benzyl alcohol oxidation over Pt/Al₂O₃ in toluene [31]. However, the decarbonylation of the aldehyde of ethanol oxidation, acetaldehyde, should then also produce CH₄ as a co-product. While the headspace analysis of ethanol oxidation indicated a small amount of CH₄ was produced in addition to CO₂, the molar ratio of CO₂:CH₄ was approximately 6.5 instead of the expected molar ratio of 1. The high molar ratio of CO₂:CH₄ after ethanol oxidation suggests that a carbon species deposited on the surface of Pt might be oxidized to CO₂ which could alter the expected ratio of CO₂:CH₄. If the headspace was exhausted after ethanol oxidation for 20 h and replaced with 3 bar H₂ at room temperature for 1 h, small quantities of methane were observed by gas chromatography. In summary, CO₂ could be produced from both the decarbonylation of an aldehyde and the oxidation of carbon-containing species on the Pt surface, but is most likely not produced by decarboxylation of an acid.

3.7. In situ ATR-IR spectroscopy

In an attempt to probe the species adsorbed on the Pt surface, in situ ATR-IR spectroscopy was performed. A review of the benefits and limitations of the attenuated total reflectance technique applied to liquid-phase systems [45] and its relevance for the investigation of heterogeneous catalysis can be found elsewhere [30]. While flat internal reflectance elements (IRE) are commonly used to investigate heterogeneous catalysts, a cylindrical ZnSe IRE was utilized in this work because it is capable of withstanding pressures above atmospheric. A drawback of the cylindrical configuration is that the amount of catalyst adhered to the IRE during dip coating is difficult to quantify. A catalyst layer that is too thick tends to decrease signal throughput, while a layer that is too thin has too few adsorption sites for detection. Also, the stability of the catalyst on the IRE surface in liquid water had to be evaluated. The Pt/C catalyst had a very low signal throughput and did not adhere well to the IRE. The ease of deposition and stability in water of Pt/SiO₂ and Pt/BN made them suitable candidates for use in the ATR-IR experiments at room temperature. A second difficulty encountered in this study was the use of water as the liquid phase. Organic solvents such as cyclohexane or toluene that are

### Table 7
Results from the oxidation of ethanol and benzyl alcohol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.69% Pt/C</td>
<td>Ethanol</td>
<td>0.15⁻¹</td>
</tr>
<tr>
<td>5% Pt/BN</td>
<td>Ethanol</td>
<td>0.17</td>
</tr>
<tr>
<td>2% Pt/SiO₂</td>
<td>Ethanol</td>
<td>0.03</td>
</tr>
<tr>
<td>2.69% Pt/C</td>
<td>Benzyl alcohol</td>
<td>0.32⁻¹</td>
</tr>
<tr>
<td>2% Pt/SiO₂</td>
<td>Benzyl alcohol</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.1 M Substrate, Sub.:Pt = 500:1 (mol:mol), T = 343 K, pO₂ = 10 bar, 0.35 M acetic acid, pH = 2.5.

* From Ref. [32].

Fig. 6. In situ ATR-IR spectra of the disappearance of benzyl alcohol (a) with H₂O saturated N₂ flowing over Pt/SiO₂ and the strong adsorption of CO on Pt (b) over 45 min at 5 bar and 298 K. The water background has been removed.

Fig. 7. In situ ATR-IR spectra of the rapid disappearance of CO after flowing H₂O saturated O₂ flowing over Pt/SiO₂ at 5 bar and 298 K. The water background has been removed.
The commonly used IR absorption peaks result in sharp and easily discernible IR absorption peaks. The IR absorption spectrum of water, however, is quite broad and significantly reduces signal throughput, both of which contribute to a low signal to noise ratio for adsorbates on catalyst surfaces. Water has strong absorption from 3700 to 3000 cm\(^{-1}\) attributed to O–H stretches, weak absorption from 2250 to 2050 cm\(^{-1}\) attributed to a combination band, and moderate absorption from 1700 to 1550 cm\(^{-1}\) attributed to O–H bends.

Fig. 5 shows the ATR-IR spectra collected after having pumped an aqueous solution of 0.1 M benzyl alcohol saturated with N\(_2\) at 1 cm\(^3\) min\(^{-1}\) at RT (298 K) and 5 bar over the 2\% Pt/SiO\(_2\) catalyst deposited on the ZnSe IRE. Results in Table 7 show that the TOF for benzyl alcohol oxidation over Pt/SiO\(_2\) in our standard semibatch reactor was similar to that of ethanol and 1,6-hexanediol (Table 2) over Pt/C, thus, benzyl alcohol was chosen as the probe molecule. The absorption bands at approximately 1004 cm\(^{-1}\) (C–O stretch) and 1212 cm\(^{-1}\) (O–H bend) in Fig. 5(a) indicate the appearance of benzyl alcohol close to the IRE surface within the probing depth of the evanescent wave. Fig. 5(b) shows an absorption band centered at approximately 2038 cm\(^{-1}\) produced during the admission of benzyl alcohol to the cell, which is assigned to the linear adsorption of CO on Pt in the presence of water. Ebbesen et al. observed a linear CO absorption feature at 2034 cm\(^{-1}\) on Pt/Al\(_2\)O\(_3\) in the aqueous phase [46]. The CO band increased with time after the introduction of benzyl alcohol to an eventual maximum after approximately 20 min. Fig. 6 shows the ATR-IR spectra as benzyl alcohol was removed from the cell by flowing only water saturated with N\(_2\). While the signal of benzyl alcohol (Fig. 6(a)) disappeared completely with time, the CO feature remained relatively unchanged (Fig. 6(b)), indicating the strong adsorption of CO on Pt.

The conditions used to generate the spectra in Fig. 5 are analogous to those in the inert startup of the semi-batch reactor experiments described earlier, except for a lower temperature in the
ATR-IR experiment. The decomposition of benzyl alcohol or
decarbonylation of benzaldehyde may have produced the CO that
was strongly adsorbed to the catalyst surface. The increase in
intensity of the peak for adsorbed CO (scans taken approximately
every minute) suggests that CO production was initially time-
dependent upon exposure to benzyl alcohol but soon reached a
maximum. The removal of the CO source (benzyl alcohol) did not
alter the signal of the CO absorption peak. Thus, the original CO
was strongly adsorbed and could not simply be displaced. How-
ever, it should be mentioned that the amount of adsorbed CO can
be difficult to quantify because the CO absorption signal is known
to be non-linear with CO surface coverage [46].

Fig. 7 shows that flowing water saturated with O₂
over Pt/BN for 10 min at 5 bar and
298 K. The water background has been removed.

Fig. 10. In situ ATR-IR spectra of the disappearance of ethanol (a) with H₂O saturated N₂ flowing over Pt/BN and the strong adsorption of CO on Pt (b) over 45 min at 5 bar and
298 K. The water background has been removed.

Fig. 11. In situ ATR-IR spectra of the disappearance of CO after flowing H₂O saturated with O₂ flowing over Pt/BN for 10 min at 5 bar and 298 K. The water background has been removed.

ATR-IR experiment. The decomposition of benzyl alcohol or
decarbonylation of benzaldehyde may have produced the CO that
was strongly adsorbed to the catalyst surface. The increase in
intensity of the peak for adsorbed CO (scans taken approximately
every minute) suggests that CO production was initially time-
dependent upon exposure to benzyl alcohol but soon reached a
maximum. The removal of the CO source (benzyl alcohol) did not
alter the signal of the CO absorption peak. Thus, the original CO
was strongly adsorbed and could not simply be displaced. How-
ever, it should be mentioned that the amount of adsorbed CO can
be difficult to quantify because the CO absorption signal is known
to be non-linear with CO surface coverage [46]. The reaction of
benzyl alcohol in a cyclohexane solvent over Pd/Al₂O₃ in an inert
atmosphere also produced a CO absorption peak from the sup-
posed decarbonylation of benzaldehyde [29]. While the C=O fea-
ture of benzaldehyde located at approximately 1700 cm⁻¹ was
not observed in this work, it may have been obscured by the very
broad absorption peak associated with water in that region. More-
ever, benzaldehyde may not remain adsorbed on the Pt surface and
instead may diffuse away from the IRE and beyond the penetration
depth of the IR evanescent wave.

Fig. 7 shows that flowing water saturated with O₂ over the cata-
lyst containing CO resulted in the complete removal of the CO,
most likely as CO₂. The oxidation of CO on a Pt surface is reportedly
faster in aqueous solution than in the gas phase over Pt/Al₂O₃ [46].
Our results suggest that any CO that is produced in the semi-batch
reactor either during the inert startup or during alcohol oxidation
with O₂ would be easily oxidized to CO₂ and therefore be removed
from the catalyst surface. Fig. 8 shows ATR-IR spectra of benzyl
alcohol solution saturated with O₂ flowing over the Pt/SiO₂ cata-
lyst. No CO was observed on the Pt surface, confirming that if
any CO were produced, it was quickly oxidized to CO₂. Thus, CO
does not appear to be a poison of the Pt surface or the cause of
Pt deactivation during the conditions of alcohol oxidation used in
this work. It should be noted that the decomposition of benzyl
alcohol or decarbonylation of benzaldehyde would produce not
only CO, but also either benzene or some carbonaceous species.

To investigate supported Pt particles on an inert support with a
demonstrated oxidation activity (Table 7) similar to that of Pt/C,
an identical in situ ATR-IR study was performed over Pt/BN using eth-
alol as the substrate. The use of boron nitride as a support elimi-
nates the interaction of hydroxyl groups, such as those found on
silica and alumina in liquid water, with the substrate. The inert
character of boron nitride might make it a more suitable support
to observe adsorbed features associated with species on Pt. Fig. 9
shows ATR-IR spectra after pumping 1 cm³ min⁻¹ of 0.1 M ethanol
solution saturated with N₂ over the 5% Pt/BN catalyst for approxi-
amately 20 min. The IR absorption bands at 2982 cm⁻¹ and
2904 cm⁻¹ have been assigned to sp³ hybridized C−H stretches of
ethanol in the proximity of the solid–liquid interface [47].

Fig. 9(b) shows the IR absorption feature of CO on Pt at approxi-
amately 2040 cm⁻¹ in the presence of water. Fig. 10(a) shows
ATR-IR spectra as ethanol was removed from the cell by water sat-
urated with N₂, whereas Fig. 10(b) shows the retention of CO on
the Pt surface even after ethanol removal. Fig. 11 shows that CO
can be rapidly oxidized from the Pt/BN using an air-saturated
water stream instead of a pure O₂ saturated water stream used
for the results in Fig. 7. The decrease in CO absorption signal with
time when air-saturated water was used, instead of the instantan-
eous removal by O₂, suggests that while the removal of CO was
still rapid, the rate of removal might depend on the concentration of O₂. Nevertheless, CO on Pt was easily removed by dissolved dioxygen, even at very low levels. Although some of the CO₂ observed during the batch-wise oxidation of ethanol over Pt/C may have originated from the CO produced by exposure to the alcohol, adsorbed CO was most likely not the cause of Pt catalyst deactivation.

4. Conclusions

The deactivation of supported Pt catalysts during aqueous alcohol oxidation was investigated at acidic and neutral conditions. A significant decrease in the oxidation rate with time was observed for both mono-alcohols and diols over supported Pt nanoparticles, regardless of the support composition or metal dispersion. Neither the leaching of Pt into solution nor the sintering of Pt nanoparticles, regardless of the support composition or metal dispersion, was significant enough to account for the observed Pt deactivation. While over-oxidation of the Pt catalyst by treatment with O₂ prior to the reaction decreased the initial oxidation rate, subsequent treatment of the oxidized catalyst with alcohol in an inert atmosphere completely recovered the activity. It is generally recognized that aldehyde condensation products can poison Pt catalysts, but under the acidic conditions of the oxidation reactions studied in this work, aldehyde condensation was negligible. Headspace analysis revealed that small amounts of CO₂ were produced during alcohol oxidation and in situ ATR-IR spectroscopy observed CO strongly adsorbed to the Pt surface after exposure of the catalyst to benzyl alcohol or ethanol. This strongly adsorbed CO was rapidly oxidized in the presence of dissolved O₂. We propose that CO was most likely formed by the decarbonylation of aldehyde intermediates, which would leave behind a remnant species on the Pt. Further investigation of the strongly adsorbed species by TGA and regeneration experiments determined that treatment in H₂ more easily removed the deactivating species compared to treatment in He. The very low deactivation of the Pt catalyst during benzyl alcohol oxidation suggests the structure of the alcohol is a key feature that determines the nature of the deactivating species formed during reaction.

Acknowledgments

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References