



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



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ABSTRACT

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- α -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 (C_xH_y) 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

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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 (H/Pt_{surf}) 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 continually 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_{surface})⁻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 4000 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, O₂, 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

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