Journal of Catalysis 326 (2015) 116–126

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Sensitivity of the glycerol oxidation reaction to the size and shape of the platinum nanoparticles in Pt/SiO_2 catalysts

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ARTICLE INFO

Article history:
Received 9 March 2015
Revised 4 April 2015
Accepted 5 April 2015
Available online 24 April 2015

Keywords:
Glycerol
Oxidation
Platinum
Selectivity
Size
Shape
Colloidal
Nanoparticles
CO titration
Infrared absorption spectroscopy

ABSTRACT

The structure sensitivity of the catalytic oxidation of glycerol with atmospheric O_2 in neutral pH water solutions was evaluated by using three series of silica-supported platinum catalysts. Transmission electron microscopy and CO titration experiments with infrared absorption spectroscopy detection were used to characterize the catalysts. Higher loadings led to larger average Pt nanoparticle sizes, but comparisons across catalysts made by different methods were unreliable because of differences in particle size distributions. Nevertheless, strong dependences of the selectivity for oxidation at the terminal versus central alcohol groups were identified as a function of both the extent of reaction and Pt particle size, with high conversions and large nanoparticles favoring terminal-carbon oxidation. Additional increases in turnover frequencies were also observed with increasing average metal nanoparticle size and with cuboctahedral versus tetrahedral Pt nanoparticles. On the other hand, no significant trends were seen in terms of further oxidation of glyceraldehyde to glyceric acid. The reported trends were ascribed to the general need for multi-atom surface Pt ensembles for conversion and to a possible unique access to the central carbonyl in glycerol only at low-coordination Pt sites.

1. Introduction

Glycerol is a primary by-product from many biofuel conversion processes, and, as a simple molecule with multiple functionalities, a promising feedstock for chemical synthesis [1–4]. Unfortunately, that promise has yet to be fulfilled. In the past, the incentive to use glycerol as a starting material was limited by its cost, and now that the price has come down, no viable selective processes are available for practical applications. In terms of the selective oxidation of glycerol (GLY), conversion at the central (secondary, C_2) carbon yields dihydroxyacetone (DHA), the main active ingredient in sunless tanning skincare preparations and other cosmetics. If a terminal (primary, C_1) alcohol moiety is oxidized instead, glyceraldehyde (GLYALD) and/or glyceric acid (GLA) is made; the latter compound is widely used in medicine because of its role as a metabolite in the glycolysis cycle and as an intermediate in the synthesis of aminoacids [1–3,5,6]. Both oxidations are desirable, but no catalytic process exists to promote either one with enough selectivity to make them commercially viable. The interest in green processes adds to the difficulty in finding catalysts for these conversions, since many of the most selective systems reported to date require extreme pH conditions [3,4].

The selective oxidation of glycerol requires some finesse, and, although many studies have been reported on the catalysis of that reaction, the results so far are incomplete and sometimes confusing. It has become clear that late transition metals are good for the promotion of these reactions, and among them, Pt (together with Pd [2,7,8], and, to a lesser extent, Au [9,10]) has been the most used to date. Both early [11–15] and more recent [16–18] studies identified a switch in selectivity with Pt-based catalysts upon the addition of Bi, which leads to a relative increase in DHA formation, but most of those studies were carried under severe pH conditions not advisable if a green process is to be developed. A number of other parameters have been shown to affect the performance of these conversions, including the nature of the support [19–21], the catalyst preparation method [9,17], the type of reactor used [11], and the reaction conditions [8] (including temperature and oxygen pressure [17]), but the information that can be extracted from the reported work is still quite limited, and no solid conclusions have been reached on these effects.

One interesting and promising factor that may control selectivity is the size and shape of the metal nanoparticles used as catalysts. In terms of metal loading, experiments with Au [22], Pd

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http://dx.doi.org/10.1016/j.jcat.2015.04.009
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[23], and Pt [7,24–27] have all suggested that large metal nanoparticles may favor the formation of glyceric acid but also lead to lower activity. Two studies have been reported on the dependence of catalytic performance on metal loading with Pt, both using carbon supports, but those have reached different conclusions [25,26]. Regarding nanoparticle shape, one study by Lin et al. [28] claimed high selectivity toward glyceraldehyde with a Pt(111)-faceted carbon-nanotube-supported catalyst, but no distinction was made between a primary oxidation selectivity at the terminal versus central carbon atoms and the likelihood of subsequent oxidation (the data suggest the latter).

Overall, the reported data are insufficient to reach solid conclusions on the effect of surface structure on catalytic activity or selectivity. In this report, we summarize the results obtained from detailed kinetic measurements made with two families of Pt/SiO_2 catalysts as a function of metal loading plus three additional catalysts with larger structures, two made by dispersing Pt colloidal nanoparticles of different shapes onto silica supports. It was found that both nanoparticle size and nanoparticle shape do play a role in defining activity and selectivity, with larger nanoparticles displaying higher reaction rates and preferentially promoting more oxidation at the terminal carbons of glycerol, and the colloidal nanoparticles displaying quite high selectivities toward glyceraldehyde production. In addition, cuboctahedral Pt nanoparticles were also determined to be more active than nanoparticles of tetrahedral shape. However, these trends are convoluted with additional effects due to the preparation method and the extent of the reaction. We further discuss these observations below.

2. Materials and methods

2.1. Catalyst preparation

Three sets of Pt/SiO_2 catalysts were prepared, two as a function of metal loading and a third using colloidal nanoparticles of different shapes. The first set was synthesized by aqueous impregnation of silica supports with $H_2PtCl_6{\cdot}6H_2O$. The precursor and support were dissolved separately in water and stirred for 30 min, and the two mixtures combined and stirred further overnight at room temperature. The water was removed by using a rotavapor set at 345 K until the solid was completely dry, and then crushed into a powder. All catalysts were calcined at 675 K under air for 4 h and reduced at 625 K under H_2 flow for 3 h before reaction. Four catalysts were prepared in this series, identified in this report as x wt% Pt/SiO_2-W, with metal loadings of $x = 0.2$, 1.0, 5.0, and 10 wt%. The second set was made in a similar fashion but using ethanol instead of water as the solvent and calcining the resulting catalysts at a lower temperature, 475 K. Three catalysts were made in this second series, denoted x wt% Pt/SiO_2-E, with metal loadings of $x = 0.2$, 0.5, and 1.0 wt%.

A third series was prepared with larger nanoparticles. One catalyst, labeled 1 wt% Pt/SiO_2-N, was prepared by using $Pt(NH_3)_4Cl_2$ as the metal precursor. This led to the formation of large and approximately round nanoparticles (see below). Two more catalysts were made by first preparing colloidal nanoparticles in solution with well-defined sizes and shapes and then dispersing those on silica supports. The synthesis was based on recipes previously used in our laboratory [29,30], which were modified from an original report by El-Sayed et al. [31]. Tetrahedral (T-Pt) and cuboctahedral (C-Pt) Pt nanoparticles were synthesized by reducing a K_2PtCl_4 precursor under the protection of polyvinylpyrrolidone (PVP, MW = 360,000) and sodium polyacrylate (SPA, MW = 2,100), respectively. 15 mL of distilled H_2O, a 1.0 mL of 10^{-6} M PVP or 0.2 mL 0.01 M SPA solution in water (for the synthesis of the T-Pt and C-Pt nanoparticles, respectively), and 0.2–0.8 g (accurately measured by using an electronic scale) of a K_2PtCl_4 solution (0.01 M in water) were mixed in a 11 dram (30 mL) vial and capped and stirred for 10 min. He gas was bubbled into the solution for 10 min while stirring, and H_2 was bubbled into the solution at the rate of 1–2 bubbles/s for 2 min. Finally, the solution was sealed and stored in the dark for at least 12 h before use. The as-synthesized colloidal particles were dispersed onto silica supports by impregnation to produce the final 1 wt% Pt/SiO_2 catalysts: The SiO_2 support was added to the vial containing the colloidal solution and the mixture stirred overnight and sonicated for 30 min, after which the solid was extracted from the solution by either vacuum filtration or rotary evaporation. The catalysts were dried in an oven at 385 K for 30 min. To remove the polymer used for the nanoparticle synthesis, the catalysts were placed in a furnace and heated to a designated temperature under O_2 flow (20–30 mL/min) for half an hour. The catalysts were then cooled down, the O_2 atmosphere was replaced by He and then by H_2, and the samples were heated again up to the same designated temperature and treated for the same length of time (30 min). Typically, this cycle was repeated three times.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) characterization of the catalysts was carried out by using a PHILIPS TECNAI 12 instrument (120 kV accelerating voltage) and Formvar/Carbon Film 400 mesh grids. Chemical probing of Pt sites was carried out by studying the adsorption of carbon monoxide on our catalysts using infrared (IR) absorption spectroscopy, as discussed elsewhere [32–34]. The data were taken in transmission mode using a Bruker Vector 22 Fourier-Transform IR (FTIR) spectrometer and a homemade quartz cell with NaCl windows capable of working at any temperature between 110 and 900 K and at any pressure between 0.01 and 1000 Torr [35–37]. A fixed amount of the catalysts, typically 10 mg, was ground in an agate mortar, pressed into a self-supporting 13 mm diameter disk, and placed inside the central holder of the reactor. It was then dried at 425 K for 1 h, either in situ under vacuum inside the transmittance IR cell or ex situ under air in a furnace, and pre-treated by following two alternating oxidizing and reducing cycles at 625 K, under 200 Torr of O_2 and 200 Torr of H_2, respectively, for 60 min each, and one final 30 min reducing treatment. Each catalyst disk was studied individually by cooling it down to below 120 K, recording the background IR trace, and exposing it to 10 Torr of CO for 5 min, after which the cell was evacuated for a minimum of 15 min. Transmission IR spectra were taken at 10-K intervals while warming up the sample, until reaching a temperature of 373 K. The infrared spectra of the adsorbed CO were recorded at a resolution of $4\ \text{cm}^{-1}$ using a mercury–cadmium–telluride (MCT) detector, and referenced to background traces recorded under similar conditions before CO adsorption.

2.3. Kinetic measurements

The glycerol oxidation kinetic studies were carried out by using a 50-mL four-neck round-bottomed flask, as described in more detail elsewhere [38]. Designated amounts of glycerol (0.20 g), distilled and deionized H_2O (10.0 g), and the catalyst (for a glycerol/Pt ratio of 1000:1) were introduced into the four-necked flask, and the system was assembled and heated to the designated temperature (typically 343 K), after which the O_2 flow (100 mL/min) was turned on and the timing of the reaction started. The solution was analyzed periodically by high-performance liquid chromatography (HPLC), using an Agilent Zorbax SAX separation column and a Linear UVIS 200 detector tuned to a wavelength of $\lambda = 210$ nm for the products and of $\lambda = 190$ nm for the glycerol detection. Approximately 0.4 mL aliquots of the reaction mixture were taken