Applied Catalysis A: General 396 (2011) 85–90

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

On the nature of the deactivation of supported palladium nanoparticle catalysts in the decarboxylation of fatty acids

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ARTICLE INFO

Article history:
Received 13 October 2010
Received in revised form 25 January 2011
Accepted 30 January 2011
Available online 4 February 2011

Keywords:
Diesel
Bio-fuel
Deactivation
Fatty acid
Bio-diesel

ABSTRACT

Supported palladium catalysts are effective catalysts for the hydrogen-free decarboxylation of fatty acids. However, the catalysts deactivate severely after one use. Here, the recyclability of a well-defined, mesoporous silica-supported palladium nanoparticle catalyst is evaluated in the batch decarboxylation of stearic acid at 300 °C under inert atmosphere, producing *n*-heptadecane. The nature of the catalyst deactivation is examined in detail via an array of characterization techniques. X-ray photoelectron spectroscopy (XPS) demonstrates that little palladium surface oxidation occurs over the course of the reaction, and a combination of X-ray absorption spectroscopy and transmission electron microscopy (TEM) suggests negligible particle sintering or agglomeration. Physisorption and chemisorption measurements demonstrate substantial loss in total surface area and porosity as well as accessible palladium surface area with these losses attributed to significant organic deposition on the catalyst, as verified via thermogravimetric analysis. High temperature calcination is applied to combust and remove these residues, but resultant nanoparticle agglomeration is significant. Solid state nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FT-IR) and solid dissolution followed by organic extraction methodologies demonstrate that the carbonaceous deposits are not coke but rather strongly adsorbed reactants and products. Detrimental coke formation, as suggested by prior literature, is verified to be absent, as extraction of the surface-deposited organic species yields nearly complete recovery of the total surface area, pore volume, and active palladium surface area. Furthermore, the regenerated catalyst exhibits a corresponding significant recovery of decarboxylation activity.

1. Introduction

In the past decade, a push to develop alternative fuels has been driven by the threat of decreasing petroleum reserves, the desire for greater domestic energy independence, and increased risk and cost in retrieving local fossil fuel reserves. Additionally, and most importantly from an environmental sustainability point of view, anthropogenic CO_2 emissions have increased the atmospheric CO_2 concentrations to significantly elevated levels [1,2]. Whether motivated by the threat of global climate change [3] or impending carbon emission regulations (tax, cap and trade, etc.), the need for viable renewable transportation fuels is greater than ever. From an economic standpoint, biofuels requiring highly refined feedstocks are simply not practical, as the cost of the feedstock alone generally eclipses that of a competitive final fuel [4]. Accordingly, much research has been put into utilizing attractive but low volume, lower-value feedstocks, such as animal by-products and other sources with high contents of fatty-acids [5]. In fact, two industrial processes have been announced in the last two years using high-acid waste streams composed of mainly animal byproducts: a ConocoPhillips partnership with Tyson to produce green diesel from chicken, pork & beef byproducts [6] and NExBTL's process for renewable diesel from plant and animal byproducts [7]. These processes, however, along with long-established hydroprocessing techniques, utilize high pressures of hydrogen to facilitate deoxygenation to paraffinic oils, increasing the operating cost of production facilities dramatically.

Recently, the Murzin group reported catalysts capable of deoxygenating long-chain acids and derivatives without the use of high hydrogen pressures or without hydrogen altogether [8–14]. Their research demonstrated that a palladium on carbon catalyst can deoxygenate free fatty acids via decarboxylation in the absence of hydrogen overpressures to form the resultant alkane. Further research on this decarboxylation reaction has been carried out

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doi:10.1016/j.apcata.2011.01.042

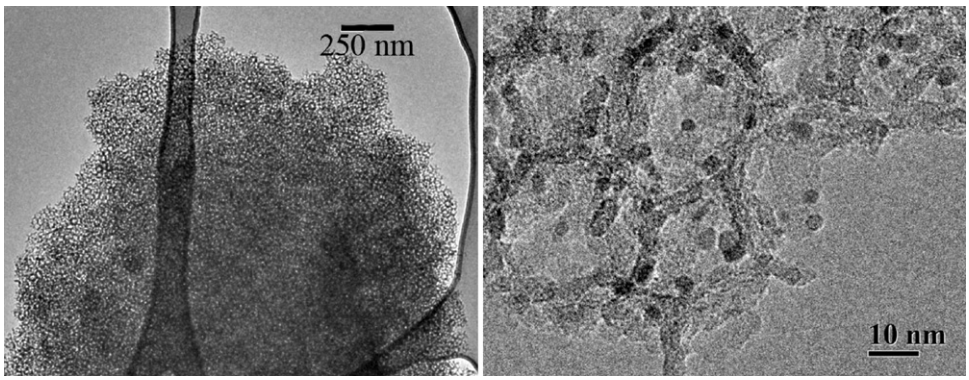

Fig. 1. TEM images of Pd-MCF catalyst showing the (a) foam-like silica substrate and (b) small Pd nanoparticles.

with continuing work from the Murzin group [15–19] and others [20–22], examining the effects of differing reaction atmospheres, temperatures, degrees of acid unsaturation, catalyst supports, and reactor types, with a wide variety of results. One observation that remains constant across the studies, however, is that the supported palladium catalysts readily deactivate during the decarboxylation reaction [12,16–18,20,22], having a detrimental effect on catalyst turnover and recycle. The trend in the literature is to recognize a decrease in catalyst surface area and pore volume, and therefore identify the most likely catalyst deactivation mechanism as coking. Although this may be a reasonable suggestion, additional evidence to support this and rule out other deactivation methods has not yet been reported.

The approach in our initial study of fatty acid decarboxylation [20] was to develop a well-defined supported palladium catalyst that could be fully characterized both before and after deactivation. A mesocellular foam (MCF) silica support was chosen to allow post-mortem carbon-based characterization techniques that would not involve significant background subtraction or interference associated with use of the commonly studied activated carbon supports. Similarly, thermal oxidative treatments such as calcination could be applied to investigate the nature of the deactivation without the potential to alter the physical properties of the support itself, as may be the case with carbon-based supports. This silica support was also designed to have very large pores to allow not only for better internal mass transfer of reactants and products during reaction, but to provide a substrate on which the nature of the reported deposition could be more easily elucidated. Finally the catalyst was synthesized in such a way to deposit a very narrow size distribution of palladium nanoparticles uniformly throughout the silica particle, yielding a well-defined catalyst on which a battery of material properties could be compared before and after reaction. Furthermore, with a small average nanoparticle size (~2 nm), various characterization techniques could be used to track not only changes in nanoparticle particle size and morphology, but the high metal dispersion would facilitate spectroscopic confirmation of alterations in nanoparticle surface oxidation or chemical poisoning. Herein we apply this catalyst (Fig. 1) to the standard literature decarboxylation reaction of stearic acid to *n*-heptadecane with the aim of (i) elucidating the nature of the deactivation and (ii) developing a procedure to regenerate the catalytic activity.

2. Experimental methods

2.1. Chemicals

The following chemicals were commercially available and used as received: dodecane (anhydrous, Sigma–Aldrich), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 95%, Sigma–Aldrich), pyridine (ACS grade >99%, Sigma–Aldrich), dichloromethane (DCM, ACS grade, EMD chemicals), stearic acid (>97%, Fluka), tetrahydrofuran (THF, ACS grade, EMD chemicals), hexane (anhydrous, Sigma–Aldrich), diethyl ether (anhydrous, Sigma–Aldrich), and potassium bromide (KBr, 99%, Alfa Aesar). Tridecane was purchased from Sigma–Aldrich, distilled over CaH_2, and stored in a nitrogen glove box.

2.2. Material synthesis

The Pd-MCF catalyst was synthesized as reported previously [20]. In this work, only the urea-functionalized precatalyst was utilized prior to metallation, mild calcination, and reduction under hydrogen flow. All samples were dried under vacuum and stored in a nitrogen glove box prior to further use in reaction or various characterization techniques.

2.3. Material characterization

Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2010. Surface area was determined by the Brunauer-Emmett-Teller method, in general using relative pressures less than 0.15. The Broekhoff-de Boer method with the Frenkel-Halsey-Hill (BdB-FHH) modification, applied first to these materials by Stucky and co-workers [23], was used to calculate pore size distributions for both the large cells (adsorption upswing, assuming spherical capillary condensation) and the interconnecting windows (desorption downswing, assuming cylindrical capillary evaporation).

A Netzsch STA409 was used for thermogravimetric analysis (TGA) under an air flow diluted by nitrogen. Samples were heated under flow at 10 °C/min from 30 to 900 °C, with the total organic content estimated from the weight loss between 150 and 800 °C. Onboard differential scanning calorimetry (DSC) was used to identify peak temperatures of combustion exotherms.

Total active metal surface area was determined by H_2–O_2–H_2 titration chemisorption measurements in a Micromeritics AutoChem II 2920. To ensure full metal reduction, samples were reduced in 5% H_2 flow at 300 °C prior to analysis with sequential titrations of H_2 and O_2. H_2 uptake at room temperature was monitored by a thermal conductivity detector (TCD), and as in previous studies [20], background uptake titrations on the bare support confirm negligible uptake from the catalyst substrate.

Catalyst dissolution was performed by stirring 250 mg catalyst in 100 mL aqueous strong base (1 g KOH/g H_2O), resulting in free palladium nanoparticles, soluble silica salts, and any residual organics. The organic fraction was separated via extractions with diethyl ether and characterized with ^{1}H NMR and GC–MS. Solution phase ^{1}H nuclear magnetic resonance (NMR) measurements were performed using a Mercury Vx 400 MHz with $CDCl_3$ as solvent.