Mesocellular Silica-supported Pd Nanoparticles for Catalytic Decarboxylation of Fatty Acids

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Introduction

Substantial attention has recently been given to developing practical fuels derived from renewable sources. Fats and oils, of which nearly 200 million tons are produced annually [1], have been identified as a candidate feedstock, but questions still remain as to their most practical conversion to fuel. Low energy density and poor cold flow properties have plagued the esterified product ("biodiesel"-- ASTM D6751), whereas the economics of standard hydroprocessing techniques have detracted from the sustainability of the deoxygenated product. Previous studies have shown zero-valent palladium is active in the decarboxylation of fatty acids and glycerides in low-H_2 environments at temperatures as low as 270°C [2]. Here we report palladium nanoparticles supported on organically-functionalized silica mesocellular foam as a viable catalyst for the decarboxylation of fatty acids.

This work describes the synthesis, characterization and kinetic activity of these supported nanoparticles for the decarboxylation of stearic acid. Various silane ligands grafted onto the surface of large pore size, ultra-large pore volume silica foam are employed to uniformly complex with the palladium precursor, and tether well-distributed nanoparticles after hydrogen reduction. Their activities are then examined as applied to the batch decarboxylation of stearic acid under an inert atmosphere.

Materials and Methods

Spherical silica mesocellular foam (MCF) was synthesized similarly to quiescent literature procedures [3,4], washed thoroughly with water and calcined in air to 550°C. For organic functionalization, the appropriate silane was added dropwise under argon to a suspension of MCF in toluene and refluxed for 48 h. The resulting solid was filtered, washed (3 x 25mL each) with toluene, acetonitrile, ethanol, and dichloromethane, then Soxhlet extracted with dichloromethane for 48 h to ensure the removal of any unreacted silane. After drying at 110°C under vacuum, the functionalized MCF was suspended in toluene, and a solution of palladium(II) acetate in dichloromethane was added dropwise to a theoretical maximum loading of 5 wt% Pd. The suspension was refluxed for 24h, filtered, washed with toluene, acetone and dichloromethane, and dried at 110°C under vacuum. Metallated catalysts were reduced prior to reaction under H_2 flow, heated to 300°C (15°C/min) for 2 h, and stored in a nitrogen glove box. Catalysts were characterized with N_2 physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), CO & H_2 chemisorption, and both scanning and transmission electron microscopy (SEM, TEM). Decarboxylation reactions were carried out in a 300°C sand bath, with 15mL pressure reactors typically charged with 25mg catalyst and 2.7mL of 0.15M stearic acid in dodecane. Reaction products were derivatized with bis(trimethylsilyl)acetamide to silylate residual carboxylic acid moeties prior to quantitative analysis via gas chromatography (GC).

Table 1. Characterization of MCF support and various catalysts.

	MCF	Pd-MCF-urea	Pd-MCF-SH	Pd-MCF-NH$_2$
SA_{BET} (m^2/g$_{SiO2}$)	840	390	660	620
d_{cell} (nm)	40	34	40	40
d_{window} (nm)	17	15	15	15
V_{pore} (cc/g$_{SiO2}$)	2.9	1.3	2.1	2.1
Ligand loading (mmol/g$_{SiO2}$)	-	2.6	0.7	1.5
d_{Pd} (nm)	-	3.0	11.8	4.1
Dispersion	-	37%	9.5%	27%

Results and Discussion

Palladium nanoparticles were formed on MCF supports functionalized with propylurea, propylthiol, and propylamine silanes. Characterization of the catalysts and bare MCF is shown in Table 1. As evidenced by the N_2 physisorption data, the functionalized and metallated materials maintain the three dimensional cell-and-window pore structure exhibited by the bare silica support, with cell diameters >34nm and interconnecting windows ~15nm. After H_2 reduction, the catalysts showed activity for the decarboxylation of stearic acid to *n*-heptadecane with 6 hour conversions of 86%, 53%, and 83%, for the urea, thiol, and amine catalysts respectively. The various methods for preparation of MCF-supported palladium nanoparticle catalysts, characterization, catalytic activity and recyclability of the catalysts will be discussed.
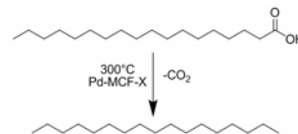
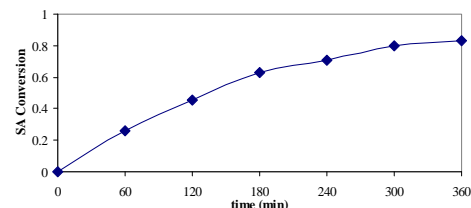**Scheme 1.** Decarboxylation of stearic acid, X: urea, SH, NH$_2$.

Figure 1. Conversion of stearic acid over Pd-MCF-NH$_2$ at 300°C.

Significance

This is a novel MCF supported palladium nanoparticle catalyst, and the first to show activity in the decarboxylation of free fatty acids. Large pore size silica supports minimize internal mass transfer limitations, while the pore geometry facilitates controlled nanoparticle growth. A sustainable decarboxylation catalyst could mitigate the current high cost of next generation biofuel production.

References

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