

The Role of Pd Dispersion in Deoxygenation of Palmitic and Stearic Acids over Pd/C Catalysts

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Introduction

Fatty acids and their esters are potential raw materials for producing long chain, diesel-like hydrocarbons, which are industrially manufactured in Finland and are known as second generation green diesel [1-3]. One of the possibilities to produce hydrocarbons is to apply catalytic deoxygenation of fatty acids and their esters over different metal catalysts.

In the current work the main aim was to systematically study the effect of Pd metal particle size and dispersion on catalytic deoxygenation of a mixture of palmitic and stearic acids.

Materials and Methods

The catalytic deoxygenation of the fatty acids (typically 0.1 M of a mixture of palmitic and stearic acids in dodecane) was performed in 300 ml semibatch reactor containing 1 g of prereduced Pd/C catalyst. The reaction temperature was varied within 260 – 300°C at pressure 17.5 bar. Liquid phase samples were withdrawn from the reactor and dissolved in pyridine in order to analyze by GC.

Four different Pd/C catalysts (A, B, C and D) supported on synthetic carbon (Sibunit) were prepared by deposition of palladium hydroxide yielded by hydrolysis of palladium chloride at pH 8-10 [4]. The different metal dispersions were achieved by changing the pH of the palladium hydroxide solution [5] (Table 1).

The fresh and spent catalysts were characterized also by BET, TEM, CO TPD and by TPR.

Results and Discussion

An optimum metal dispersion (47-65%) was found, which was giving the highest catalytic activity in palmitic and stearic acid deoxygenation (Table 2). As one can expect large Pd particles in a sample A are not enough active due to their relatively small surface area. On the other hand highly dispersed Pd species in a sample D are not sufficiently active because of their strong interactions with the support resulting in the changes of Pd metal structure required for effective deoxygenation of stearic and palmitic acids. The presence of small Pd particles in the samples B and C provides enough high surface concentration of active Pd atoms in the proper metal structure.

Table 1. Pd particle size determined by CO chemisorption and by TEM analysis.

Catalyst	state	d _{CO} (Pd), nm Pd particle size determined by CO chemisorption	d _{TEM} (Pd), nm Pd particle size determined by TEM, mean	Metal dispersion (%)
A	Spent	6.2	6.1	18
B	Spent	2.8	3.1	47
C	Fresh	1.7	2.3	65
D	Fresh	1.6	2.8	72

Table 2. Kinetic data for different 1 wt.% Pd/C catalysts in stearic and palmitic acid (SA) deoxygenation at 300°C and 17.5 bar H₂/Ar. Catalyst mass 1 g.

Catalyst	Initial rate (mmol/ min/g _{cat})	TOF (s ⁻¹)	Conversion after 300 min	Selectivity to n-heptadecane at 50% conversion (%)	Selectivity to n- heptadecane at 95% conversion (%)
A	0.03	30	68	98	a
B	0.2	79	100	99	99
C	0.4	109	99	99	99
D	0.05	12	96	98	98

^aonly 68% conversion was achieved within time of experiment.

Significance

The data obtained in the current work could be applied for the design of new effective catalysts for green diesel production.

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