Catalyst Design for the Hydrogenation of Cinnamic Acid to Hydrocinnamic Acid.

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Introduction

3-Phenyl-2-propenoic acid, or cinnamic acid, is a white crystalline solid having a low intensity sweet, honeylike aroma [1]. It serves as a precursor for derivatives, such as esters which have pleasant long-lasting aromas [3] and methyl cinnamate which is used in the flavor and fragrance industry in products like soaps, cosmetics, beverages, baked goods, and convenience foods [1]. Another application for cinnamic acid and its derivatives include light penetration inhibitors in sunscreen formulations [4]. Hydrogenation of cinnamic acid under mild conditions leads to 3-phenylpropanoic acid, or hydrocinnamic acid [2]. Since it is widely known that Pd catalysts hydrogenate double bonds well without affecting other functional groups, this hydrogenation reaction can be used as a quick activity measure for heterogeneous Pd catalysts. We investigated the effects of different carbon supports using reduced and unreduced Pd catalysts on the hydrogenation of cinnamic acid to hydrocinnamic acid.

Materials and Methods

Catalysts were prepared by Evonik proprietary methods using carbon supports based on wood (steam and phosphoric acid activated), peat, and coconut. All catalysts were prepared at 5% Pd loading. Each support was used to prepare two catalysts – one reduced and one unreduced - in order to compare which Pd state performs better in this reaction. The hydrogenation reaction was carried out in a stirred tank reactor at 25°C and 10 millibars. A mixture of cinnamic acid, ethanol, and catalyst (150mg) were added to the reactor. Hydrogen uptake is measured after an initial offset time (3min) and the recorded activity is the amount of hydrogen consumed in a fixed time (5min). The reaction mixture was collected and analyzed by GC to confirm conversion and selectivity data. Catalysts were also characterized for Pd dispersion using Micromeritics AutoChem 2910. Surface area and pore size distribution of carbons was determined by Micromeritics ASAP 2405.

Results and Discussion

Table 1 shows the results of the surface area and pore volume measurements for the carbons used to make the catalysts, as well as catalyst characterization results. It can be seen that there are some clear differences in the surface areas and pore volumes that might impact the activity of the catalyst. The selectivity toward hydrocinnamic acid as determined by gas chromatograph for each catalyst was 100% at our test conditions. Figure 1 shows the correlation between activity and conversion as measured in the gas chromatograph.

Significance

The data collected from the various experiments suggests that unreduced Pd catalysts are more active and have a higher conversion than reduced Pd catalysts. We can also see that the Pd catalysts made with coconut carbon tend to have the lowest activity and conversion. As the micropore volume and average pore diameter of the coconut carbon is much different than the other carbons, diffusion-limiting properties could be the reason for the lower activity and conversion. The metal dispersion of the catalysts cannot predict the conversion alone, but can serve as useful information when coupled with activity data. The activity test data provided the best correlation of conversion from cinnamic acid to hydrocinnamic acid. This method is a quick and easy test to predict conversion without the need of using a gas chromatograph. In summary, the choice of activated carbon support and the preparation method have a great impact on catalyst activity in the given reaction.

Catalyst	Carbon	Carbon Source (Activation)	BET Surface Area [m²/g]	Total Pore Volume [cc/g]	Micropore Volume [cc/g]	Average Pore Diameter [A]	Catalyst Type	Metal Dispersion [%]	Activity [mLH_2/g_{cat}*min]	Conversion [%]
A1	A	wood (steam)	910	0.73	0.2	25	reduced	23	782	60
A2							unreduced	27	1109	74.7
B1	B	wood (H_3PO_4)	1478	1.27	0.07	34	reduced	15	688	56.2
B2							unreduced	25	1061	70.5
C1	C	peat	878	0.63	0.23	22	reduced	24	729	60.1
C2							unreduced	24	1000	
D1	D	coconut	1609	0.82	0.41	16	reduced	12	127	24.5
D2							unreduced	16	485	38.1

Table 1. Carbon and catalyst characterization results.

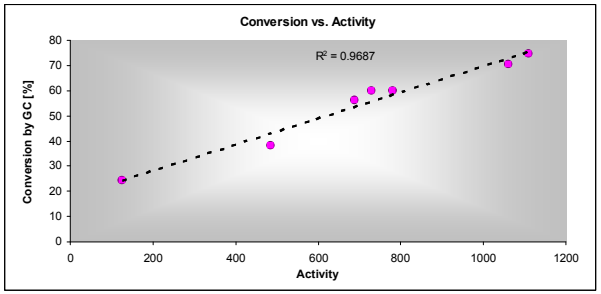

Figure 1. Conversion vs. Activity correlation.

References

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