The Influence of Reducing Agents on Palladium Crystallite Size and Distribution on Activated Carbon Catalysts

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Introduction

The crystallite size and distribution of precious metals on activated carbon catalysts play a key role in achieving high activity and selectivity. This is especially evident in reactions with larger molecules at ambient temperatures and pressures. In an effort to reduce diffusion limitations, the precious metal can be deposited onto the outer layer of the carbon surface in an eggshell distribution. However, it was observed that during preparation of reduced, eggshell catalysts the reductant affected the final precious metal distribution [1]. This reductant-induced Pd migration was investigated in this study.

Materials and Methods

Oxidic, eggshell 10% Pd/C catalysts (A1, A2) were prepared by an Evonik proprietary method. Several 10% Pd reduced-type catalysts were made based on this recipe. The only difference between catalysts B1, C, D, E and F was reducing agent used.

The hydrogenation of the cinnamic acid (**CA**, 98+% purity) was carried out in a low-pressure test unit where the temperature was kept at 25°C with a constant agitation speed of 2000 rpm. In a typical reaction run, a solution of 10g of solid CA dissolved in 80 mL of ethanol (99.8+% purity) and 100 mg of dry 10% Pd/C catalyst was added to the reactor, followed by 40 mL of ethanol for rinsing. The mixture was stirred under a constant pressure of 10 mbar of H_2.

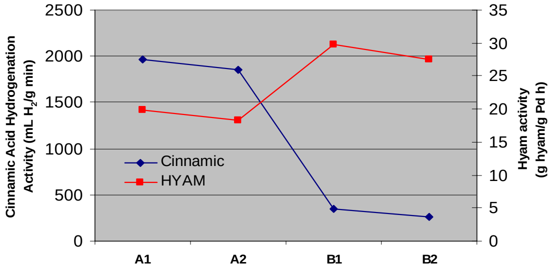
In a typical test of HYAM activity, 750 mg of catalyst was added to a continuous stirred tank reactor containing the nitrate ions in 1L of phosphate buffer solution. This suspension contained 85% H_3PO_4 (331 g), $NaNO_3$ (198 g), NaOH (84g), and GeO_2 dissolved in water and was stirred under a H_2 flow of 150 L/h. The amount of HYAM formed after 90 min at 30°C was measured by titration [2-3].

Results and Discussion

All catalysts were characterized by the hydrogenation of CA (model large molecule) and of nitric acid to hydroxylamine (model small molecule) as well as CO chemisorption. Some were also characterized by TEM.

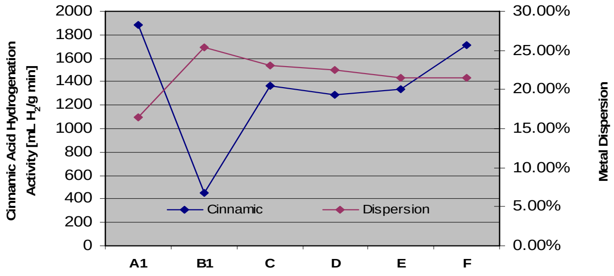
The results obtained upon wet reduction of an eggshell Pd/C catalyst suggested that metal migration occurred. In Figure 1, catalysts A1 and A2 (oxidic, eggshell) exhibit a high CA activity and a lower HYAM activity. It is hypothesized that eggshell catalysts are more active for CA because of its diffusion limitations. The active Pd sites are located on the carbon surface where the CA has no diffusion limitations. However, in the HYAM test, catalysts A1 and A2 are less active, possibly due to either to nitric acid's ability to easily diffuse further into the carbon support where little to no active Pd surface area is available or due to the poor solubility of H_2 in aqueous reaction media. Catalysts B1 and B2 (reduced A1 and A2) exhibit the opposite trend, suggesting that during wet reduction the Pd metal migrated further inside the carbon support to form a more uniform metal distribution. TEM supported these results.

Figure 1. Cinnamic Acid and HYAM activity



Several catalysts (C-F) were prepared using other reducing agents. Figure 2 indicates that the reducing agents caused Pd metal migration. From the lower CA activity and higher metal dispersion, it is hypothesized that reductions of catalysts C, D and E produced a thick-eggshell Pd distribution. Catalyst F exhibited the CA activity traits of an eggshell catalyst with the metal dispersion of a uniform catalyst. TEM of these catalysts will be presented as further evidence to support these hypotheses.

Figure 2. Cinnamic Acid and Metal Dispersion of catalysts A1 - F



Significance

Reducing agents can influence the Pd metal distribution on activated carbon catalysts. Depending on method and reductant used, Pd migration depth can be customized for a particular reaction.

References

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