

## Microscopy and Reactivity of Commercial Benzene Hydrogenation Catalysts after Years On-Stream

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### Introduction

Benzene hydrogenation to produce cyclohexane is a high-volume, demanding commercial application due to the need for extremely high selectivity (e.g., avoid methyl cyclopentane formation) in an exothermic environment. Both heterogeneous and homogeneous catalysts can be used for the reaction; heterogeneous catalysts had been historically dominant, though this has shifted in recent years with homogeneous catalysts taking a significant position. However, even in new installations with homogeneous catalysts, heterogeneous catalysts are still used in polishing reactors.

Typical heterogeneous catalysts contain either Pt, Pd or Ni supported on alumina. Over time, catalyst performance as measured by both rate and selectivity declines; catalysts are replaced, and the precious metal recovered, typically every 3 or 4 years. It is therefore interesting to study commercial benzene hydrogenation catalysts which have been on-stream for a number of years in an attempt to understand the root cause of the decline in performance.

### Materials and Methods

Samples of a Commercial benzene hydrogenation catalyst (0.75 wt-% nominal Pt) in both a fresh state and after being used for several years in a multi-bed commercial reactor were obtained and investigated. The catalysts were characterized by a variety of techniques, including scanning transmission electron microscopy (STEM, HB-601UX microscope), temperature programmed reduction, hydrogen chemisorption and other various chemical and physical analyses. In addition, the activity and selectivity of the catalysts were investigated using common laboratory probe reactions such as methyl cyclohexane dehydrogenation, toluene hydrogenation and ethane hydrogenolysis. Commercially used catalysts were reactivated using an very mild laboratory regeneration procedure prior to analysis.

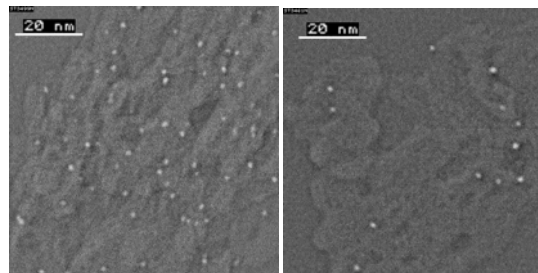
### Results and Discussion

The Pt content (determined by ICP) and the surface area of the catalysts were evaluated. These results showed that no loss of Pt had occurred during the operation and that only a very small but consistent decrease in the surface area of the catalyst had occurred. From evaluations of other catalysts, it was determined that this minor decrease in surface area was not sufficient to explain the deterioration in the catalyst performance which had been observed commercially.

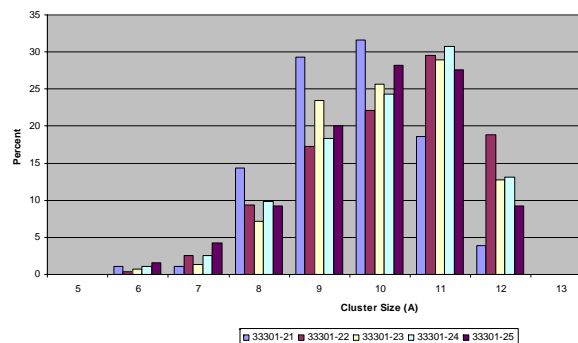
Analysis of the fresh and spent catalysts by STEM initially revealed only subtle differences in the average size and distribution of Pt particles on the catalyst surface. Figure 1 shows a low-magnification image of the Pt particles on the alumina support in the (a) fresh catalyst and (b) commercially used catalyst. Particles are very similar in size in both, ranging from 6 to 10 Å in the fresh sample and from 6 to 12 Å in the commercially used sample.

A sufficient number of Pt particles were identified through image analysis to obtain a statistically relevant representation of the overall Pt particle size distribution on the catalyst samples. This analysis, shown in Figure 2 and as mean cluster sizes in Table 1, identifies a

clear shift to larger particle sizes upon commercial use (as expected). However, the magnitude of the mean particle size shift is quite small (9.6 to 10.1 Å). It is notable that the density of the largest particles (12 Å) has increased by a factor of 2 or 3 times on the commercially used samples versus the fresh material.



**Figure 1.** STEM images of fresh (a) and commercially used (b) catalysts.



**Figure 2.** Particle size distributions of Pt as determined by STEM image analysis.

Catalyst	33301-21	33301-22	33301-23	33301-24	33301-25
Description	Fresh	Reactor A1	Reactor A2	Reactor B1	Reactor B2
Mean Particle Size (Å)	9.6	10.2	10.1	10.1	9.9

**Table 1.** Catalyst descriptions and mean particle size observed.

### Significance

Analyses by TPD and H<sub>2</sub> chemisorption showed more noticeable differences in these catalysts while, interestingly, all probe reactions showed essentially equivalent performance of all catalysts. Possible reasons for the difference in the commercial observation and the laboratory observations include the use of the laboratory activation procedure and the potential presence of other (contaminants) on the catalyst. Evidence for these will be presented and discussed in detail.