The origin of metal loading heterogeneities in Pt/zeolite-Y bifunctional catalysts

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Bifunctional zeolite-based catalysts are of great importance for production of high-quality fuels and chemicals from alkane feedstock. In these bifunctional catalysts, metal sites perform (de)hydrogenation of alkanes/alkenes, while zeolite acid sites carry out skeletal rearrangements such as isomerization and cracking. Along with metal and acid functions, other properties such as high thermal stability make zeolite-based catalysts essential for e.g. oil refineries.

Besides metal loading and size of metal nanoparticles, research has shown that the ratio between metal and acid sites is highly important for the catalytic performance of bifunctional catalysts. It also was shown that in Pt/zeolite-Y catalysts prepared with incipient wetness impregnation (IWI), variation in metal of 0.2-7 wt% Pt occurred between individual zeolite crystals of the same catalyst batch with a nominal loading of 1 wt% Pt. Such large heterogeneities can potentially have adverse effects on activity and selectivity of the catalysts. Therefore, it is important to understand the origin of the nanoscale heterogeneities in Pt loading in order to be able to optimize the catalyst synthesis and performance.

In this research, we used ion exchange (IE) and IWI methods to prepare Pt/zeolite-Y catalysts using commercially available Zeolyst CBV760 (steamed and acid-leached zeolite) and Pt(NH\textsubscript{4})\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} precursor. For both synthesis methods different bulk loadings of platinum metal were prepared (0.5 wt% to 3.0 wt%), confirmed by ICP measurements. Scanning transmission electron microscopy (STEM) was used to identify platinum particle size, which was on average 1.7 nm in diameter (Figure 1a) and in line with results obtained by H\textsubscript{2}-chemisorption. Transmission electron microscopy energy-dispersive X-ray (TEM-EDX) spectroscopy was performed on individual zeolite crystals, to determine the Pt loading and the Al/(Si+Al) atomic ratio of individual crystals. The latter is often linearly related to the amount of acid sites. A clear correlation between Pt weight loading and the Al/(Si+Al) ratio was found for IE prepared samples (Figure 1b). IWI prepared samples show similar correlations (Figure 1c), though with more scattered data points. Importantly, large differences in Al content per zeolite crystal within the same sample were observed. It was hypothesized that heterogeneity in Al content was introduced by post-synthesis treatments of zeolite Y. EDX studies of pristine, steamed, steamed and acid-leached zeolite Y samples showed that post-synthesis treatments can greatly influence Al content per crystal, indicating that post-synthesis treatments affect zeolite crystals to a different extent.

![Figure 1 a: STEM images of two different crystals within the IE-1.3 sample. Scale bar is 20 nm. Bright spots indicate the Pt metal nanoparticles. Clear differences in Pt loading can be observed for the two crystals. The image is representative for IE prepared samples as well as IWI prepared samples. b: EDX quantification results for Al and Pt measurements of individual crystals for IE prepared samples with different overall (1.3-2.4 wt% Pt) loadings. c: EDX quantification results for IWI prepared samples with different loadings (0.9-2.8 wt% Pt).](image)


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