Utilization Of EDX Chemical Maps To Understand Coke Formation In Reforming Catalysts

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Ever increasing demands to understand catalytic materials at atomic length scales have led to more complex problems requiring more advanced analytical tools. Common topics of study encountered in heterogeneous catalysis, for example, are the importance of electronic and atomic structure of the metal clusters[1], metal species mobility[1], catalyst stabilization by the addition of secondary metals [2], and lastly, studies involving coke development [3]. Among the topics listed the latter subject is important since excessive coke formation can ultimately lead to catalyst deactivation [4]. In this study we look to understand the coking mechanism via chemical mapping by examining Pt-Re/γ-Al$_2$O$_3$ catalysts prior- and post-deactivation in a reforming pilot plant. Here we show, for the first time, visual characterization of coke on a spent catalyst and derive aspects of coke formation.

The Pt-Re/γ-Al$_2$O$_3$ reforming catalyst (0.35 wt % Pt and 0.25 wt % Re and 0.06 wt % S) was pilot plant tested for both 10 and 96 hours. Combustion analyses of the spent catalysts revealed an accumulation of 0.6 wt % (10 hour) and 10.6 wt % coke (96 hour). Scanning transmission electron microscopy (STEM) analysis of the spent (and fresh versions of the catalyst) showed a small, but noticeable increase in cluster size with time-on-stream (TOS) from 7.4 Å to 7.8 Å (Figure 1). Changes to the Pt-Re stoichiometry of the clusters were also monitored during chemical analysis. Energy-dispersive X-ray spectroscopy (EDX) of individual clusters revealed a broadening in the distribution of Pt:Re ratios over time resulting in a net increase in Re richness with TOS.

Chemical mapping was carried out for the two spent catalysts to evaluate how the coke formed on the catalyst. For the 10 hour sample (0.6 wt %) the C chemical map appeared to show a uniform coating of coke over the catalyst (Figure 2). As can be seen from the combined chemical map (Figure 1b) the carbon levels (C, green), on the γ-Al$_2$O$_3$ (Al, red), are only slightly above background. Arrows on the chemical map point to locations on the γ-Al$_2$O$_3$ where Pt-Re clusters reside. No apparent trend was observed with respect to the position of the clusters and the formed coke for the 10 hour sample. However, it was frequently noticed that even at low levels there was a tendency for the coke to fill the porous regions of the support. This can be clearly observed by comparison of the low density regions of the γ-Al$_2$O$_3$ (Figure 2a) with corresponding regions in the chemical map (Figure 2b) in which the C signal is higher in the low Al signal regions.

Similar analyses were carried out for the 96 hour spent sample. In contrast to the 10 hour sample, the 96 hour sample showed heterogeneous dispersions of coke on the catalyst (Figure 3). These heterogeneous coke deposits are likely on top of the thinner, more uniform coke coverage seen in Figure 2b. A correlation was identified between formed coke and location of the metal function (arrows in Figure 3b). The trend found in the chemical maps supports the theory of coke streaming from metal to catalyst support [4]. These more substantial deposits of coke were non-uniform and they emanate from the metal sites. This is the first chemical map of which we know showing both coke and metal clusters as they exist on a reforming catalyst. The alignment of these data with theory will be discussed.
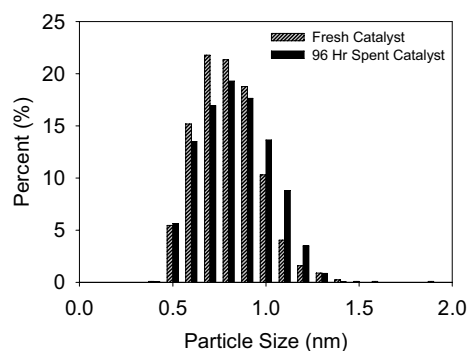
Figure 1. Size distribution histograms comparing the fresh and 96 hour spent Pt-Re/γ-Al$_2$O$_3$ catalyst.
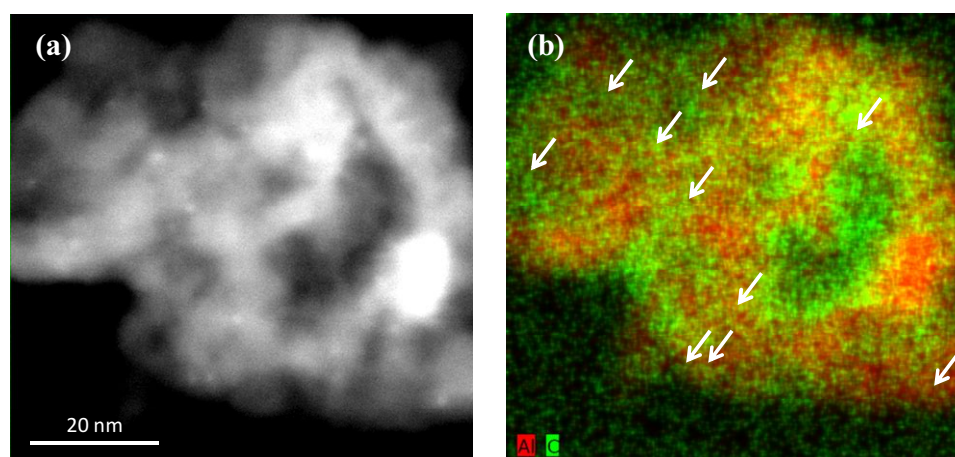
Figure 2. (a) STEM micrograph of 10 hour spent Pt-Re/γ-Al$_2$O$_3$ and (b) corresponding Al and C chemical map. The ends of arrows in (b) designate the location of the clusters found in (a).
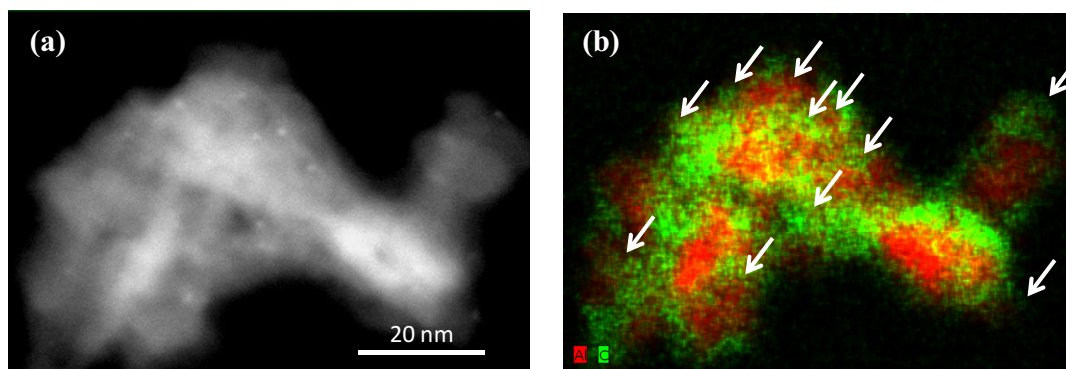
Figure 3. (a) STEM micrograph of 96 hour spent Pt-Re/γ-Al$_2$O$_3$, with (b) corresponding Al and C chemical map. The ends of arrows in (b) designate the location of the clusters found in (a).

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