Nanoscale Chemical Imaging of Zeolites Using Atom Probe Tomography

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Abstract: Understanding structure-composition-property relationships in zeolite-based materials is critical to engineering improved solid catalysts, but can be difficult to realize as complexities span several orders of magnitude, with consequences for reactivity, diffusion and stability. Atom Probe Tomography (APT) is the only technique so far capable of producing 3-D compositional reconstructions with sub-nm-scale resolution, and has only recently been applied to zeolite-based catalysts. We demonstrate APT to study zeolites, and will focus on methanol to hydrocarbons (MTH) reacted ZSM-5 and SAPO-34, as well as the deNOx catalyst Cu-SSZ-13, and give nanoscopic insights found in these materials.

Keywords: Zeolites, Atom Probe Tomography

1. Introduction

Innumerable studies have produced many insights into structure-composition-property relationships in zeolite-based catalyst materials across many length scales, and this effort is made to engineer superior solid catalysts, while working within the constraints of manufacturing, material limitations and ultimately economic drivers. A wealth of fundamental knowledge has been gained, but still with a significant gap in achieving 3-D chemical reconstructions at sub-nm scale resolution, as techniques that offer sub-nm length scale information mainly give only bulk averages, and those that offer spatially resolved information, e.g. TEM, have difficulty in differentiating the primary zeolite elements (i.e., Al, P and Si) due to their close and light atomic masses. Atom Probe Tomography (APT) is uniquely able to provide such information as it is the only technique today capable of creating 3-D elemental reconstructions of materials with sub-nm scale resolution and unambiguous elemental identification. Herein, we will discuss the technical details to apply APT to zeolites including sample preparation, APT data collection as well as details of the data analysis. Furthermore, we will highlight nanoscopic insights gained in these catalysts, especially regarding coking and deactivation from the MTH reaction and aging of Cu-exchanged $deNO_X$ catalysts.

2. Experimental

The technical aspects of using APT to study zeolites are extensively discussed in our recent manuscripts including sample preparation, APT experiment and data analysis.[1–5] All APT experiments were conducted at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

3. Results and discussion

APT has been applied for decades to study conductive materials, especially metals, and recent advances in the technique now allow it to be used to study nonconductive materials as well, motivating us to apply the technique to zeolites. Although significant

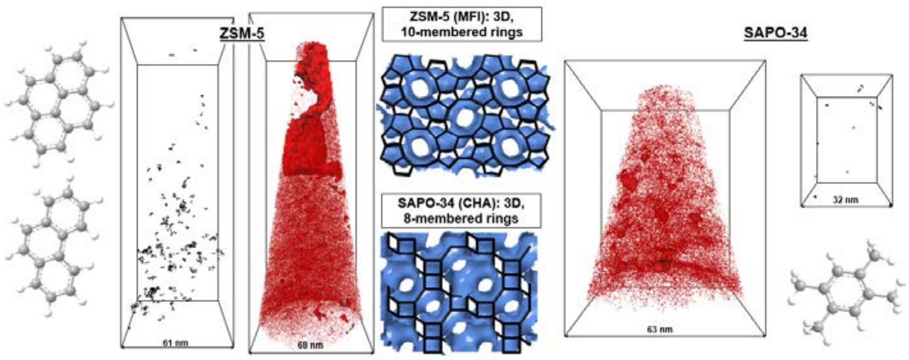

Figure 1. A comparison of the significant differences in coking behavior identified by atom probe tomography (APT) in ZSM-5 and SAPO-34. APT has determined that the ZSM-5 framework contains coke depleted regions on length scales of tens of nanometers while in SAPO-34 there were no coke depleted regions. Cluster analysis identified many coke carbon clusters in ZSM-5, with sizes consistent with polycyclic aromatic species, and two possible coke molecules are shown that are of a size consistent with the carbon clusters (note APT does not provide molecular fingerprinting). In SAPO-34 only a few, small coke carbon clusters were identified, consistent with the smaller pores of this material preventing the formation of numerous polycyclic aromatic species.

technical challenges exist in all aspects of the measurement due to the highly heterogeneous, nonconductive nature of zeolites, several successful studies have been recently published by our group and others.[1–8] We have used APT to study ZSM-5 crystals that were coked in the methanol to hydrocarbons (MTH) reaction, and compositional heterogeneities were identified on multiple length scales, as is shown in Figure 1.[1,2] Regions depleted in coke were identified which did correlate with any change in Brønsted acid site density (Si/Al ratio), pointing to the possibility of internal diffusion barriers. Further, with cluster analysis, we could identify clusters of coke carbon that were of a size consistent with polycyclic aromatics, known coke molecules, and further analysis revealed that they exist around regions that are nanoscopically enriched in Al, demonstrating a nanoscopic relationship between local increases in acid site density and the formation of detrimental coke species. When SAPO-34 was investigated, no coke depleted regions were identified, and only a few small carbon clusters were found, that were also shown to correlate with an increase in Brønsted acid site density, as found in ZSM-5, and the smaller cluster size is consistent with differences in the frameworks between SAPO-34 and ZSM-5, shown in Figure 1.[5] We have also invested Cu-exchanged zeolites used for $deNO_X$ catalysis, Cu-SSZ-13 and Cu-ZSM-5. As shown in Figure 2, Cu-SSZ-13 is only slightly degraded after a 135,000 mile aging simulation, while Cu-ZSM-5 experiences severe degradation due to the formation of a copper aluminate spinel phase ($CuAl_2O_4$) that non-selectively oxides ammonia and degrades catalytic performance. Overall, gaining a complete picture of the deactivation of a catalyst material though atom-by-atom 3D reconstructions provides key information that industry needs to design better catalysts.

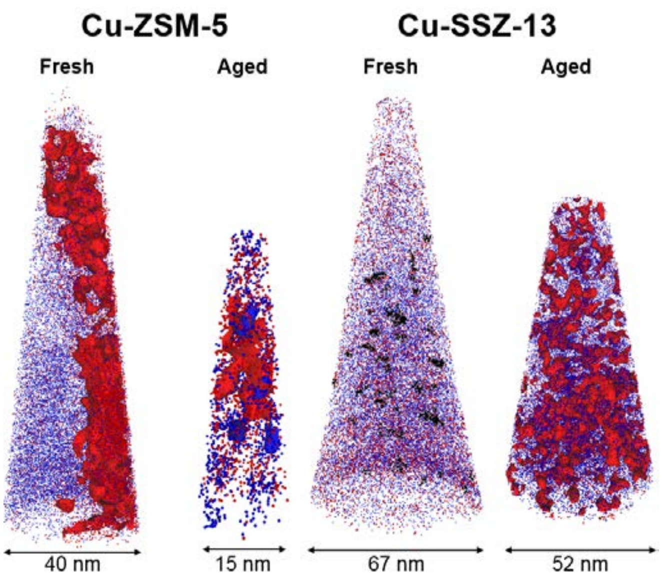

Figure 2. Reconstructions of two zeolite catalysts (Cu-SSZ-13 and Cu-ZSM-5) used in diesel-vehicle catalytic converters (Al in blue and Cu in red). The catalysts are fresh or aged (135,000 miles of diesel engine exhaust simulation). After long-term aging, the Cu-SSZ-13 catalyst still cleans exhaust well while the performance of Cu-ZSM-5 is highly degraded. Atom-by-atom 3D reconstructions reveal that the degradation of Cu-ZSM-5 is due to the formation a deleterious phase, $CuAl_2O_4$.

4. Conclusions

APT shows exciting potential to gain insights not only into zeolites, but to heterogeneous catalytic materials in general. We have demonstrated its application to a wide range of zeolites to gain nanoscale correlations into coking from the MTH reaction as well as the degradation of deNOx catalysts. Moreover, we believe in the future that APT will experience broader use in the characterization of heterogeneous catalysts due to its unique capabilities.

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