

Quantification of Elemental Spatial Correlations in Commercial Automotive Catalysts

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Introduction

Heterogeneous catalysts have been successfully applied for automotive exhaust aftertreatment. Increasingly stringent emission regulations and rising cost of precious metals are driving current effort to further improve both well-established three-way and emerging diesel catalysts [1]. Fundamental catalyst characterization is important in the development of catalysts. However, quantitative analysis of real-world catalysts is difficult due to complex compositions and structures. For example, the active phase (“washcoat”) of a three-way catalyst is a mixture of various components: precious metals (Pt, Pd, Rh), supports (Al_2O_3 , TiO_2), oxygen-storage materials (CeO_2 - ZrO_2), and dopants (La, Ba). The Lean NO_x Trap (LNT) incorporates NO_x storage materials (Ba, K) to three-way catalyst to be effective under lean-burn conditions. Non-uniform spatial distribution of components (e.g., layered washcoat structures; composites of compositionally distinct domains) further complicates analyses. Finally, over the course of their useful life, the catalysts are exposed to different deactivation mechanisms (e.g., poisoning, thermal aging) which can affect different catalyst functions over the domains of the catalysts. Understanding and quantifying the elemental distributions of catalytic components and their response to diverse deactivation mechanisms is important for developing catalysts and models. In this work, we developed simple numerical methods of quantifying the coincidence and the correlation lengthscales of different elements using electron probe microanalysis (EPMA) of commercial automotive catalysts.

Materials and Methods

A fresh three-way catalyst and a sulfated LNT were analyzed to demonstrate our methodology. Sections of monolithic cores were used for EPMA after applying epoxy and polishing. The EPMA imaging was performed using a Jeol JXA-8200 SuperProbe, and images representing the relative intensity of a given element at each pixel (probe-spot location) in an x-y grid, was produced for various elements. Figure 1 shows sample images for an LNT section.

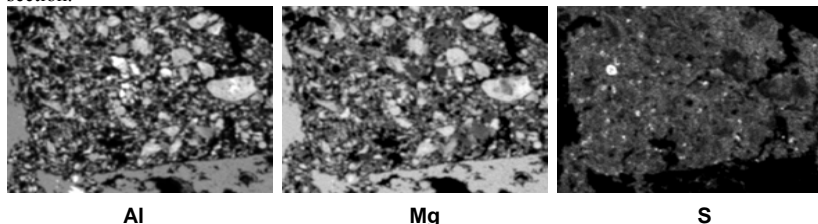


Figure 1. EPMA intensity images of an LNT cross-section for Al, Mg and S. The dark borders in the S image help define the borders of the cordierite.

For each pair of element images X and Y , a cross-correlation coefficient was calculated:

$$C_{X,Y} = \langle X(i,j) \cdot Y(i,j) \rangle / (\sqrt{\text{var}(X) \cdot \text{var}(Y)})$$

where i and j are pixel indices, the denominator normalizes C in $[-1,+1]$, and X and Y are centered to have zero mean. Values of C close to 1 indicate strong correlation (i.e., elements are found together at the same probe location), and negative values indicate anti-correlation (i.e. they are less likely or well below expected to be found together at the same probe location).

Results and Discussion

The correlation coefficients for select elements (Fig. 1) are depicted in Fig. 2. Based on bulk analyses (ICP), the fresh LNT comprises Pt, Pd, Rh, Ba, Al, Mg, Ce, and Zr as major components. Our analyses reveal that Al, Mg and O strongly correlate, and somewhat anti-correlate with Ce and Zr (Fig. 2). On the other hand, Ce and Zr show a strong correlation each other and also with Pt, Pd, Rh, and Ba (results not shown). It follows that this catalyst is a composite of two distinct domains: MgAl_2O_4 and Pt/Pd/Rh/BaO supported on CeO_2 - ZrO_2 . Sulfur poisoning tends to be more evenly spread but is most strongly correlated with Ba.

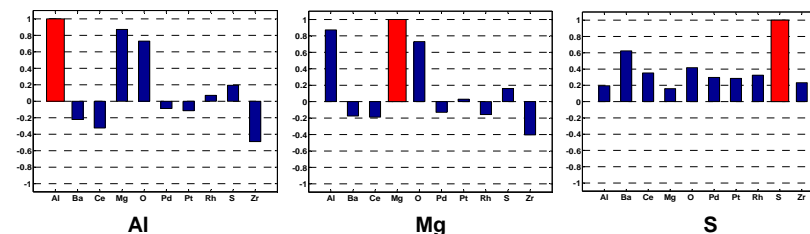


Figure 2. Correlation coefficients for Al, Mg and S against other elements for the sulfated LNT section (Fig. 1). Red bars represent self-correlation (for visual reference) and blue bars cross-correlation. Al, Mg and O are highly correlated and show similar patterns of anti-correlation with other elements, whereas S most highly is associated with Ba.

Comparing sections from the channel inlet and outlet show that while the elemental correlations within the washcoat materials do not change significantly, the distribution of sulfur changes. This sulfur trend is consistent with the catalyst performance trend [2]. In this presentation, after detailed analyses of two catalytic systems, we will discuss how this methodology can be extended to provide correlation lengthscales to determine on how distributed or clustered coincidental elemental concentrations are.

Significance

This work provides direct quantification of the spatial correlations of elements not attainable with bulk elemental analysis. The results are useful to understanding how real automotive catalysts work across the channel domain and for developing models.

References

1. Twigg, M.V., *Appl. Catal. B*, 70, 2 (2007).
2. Choi, J.-S., Partridge, W.P., Pihl, J.A., and Daw, C.S., *Catal. Today* **136**, 173 (2008).