Experimental Investigation and Kinetic Modeling of Diesel Oxidation Catalysts for Emissions Aftertreatment from Diesel Engine Exhaust

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Keywords
Diesel engine exhaust, Emission oxidation, Diesel oxidation Catalyst (DOC), microkinetic modeling

Emissions from the diesel engine is one of the major concerns for global warming, human health and environmental pollution, due to many toxic and harmful exhaust gasses like carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur oxides (SO_x) and many other volatile organic compounds (VOCs) [1] and poly aromatic hydrocarbons (PAHs) [2]. Diesel Oxidation Catalyst (DOC) is a predominant component in emissions aftertreatment to meet such regulations [3]. As shown in Figure 1a, In Urea- or aqueous ammonia-based Selective Catalytic Reduction (SCR) of NO_x, the Pt/Pd based DOC is typically placed upstream of the SCR to achieve an optimum NO: NO_2 ratio for improved SCR efficiency. On the other hand, as shown in Figure 1b, in HC-based SCR (e.g., using Diesel/ethanol/mixtures), a downstream DOC would be required to oxidize the toxic byproducts, such as CO, ammonia (NH_3), formaldehyde (HCHO), hydrogen cyanide (HCN), acetonitrile (CH_3CN), and acetaldehyde (CH_3CHO), to relatively 'less' harmful CO_2 and NO_x.

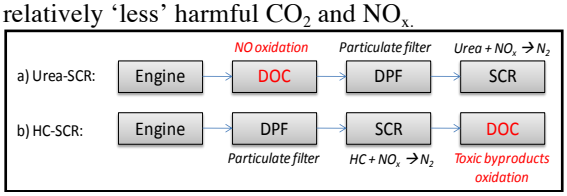


Figure1 *Role of DOC in toxic emissions oxidation.*

The noble metal based DOC is one of the most expensive components of the emissions aftertreatment system, and is typically overdesigned to some extent to ensure complete oxidation of toxic byproducts. Despite the extensive research conducted on DOC performance, comprehensive and predictive kinetic models for simultaneous catalytic oxidation of multiple emissions are limited due to the complex multi-species interactions.

In this work, we have developed a detailed elementary-step microkinetic model for DOC that accounts for (i) CO oxidation, (ii) NO oxidation, (iii) oxidation of other N-containing emissions, such as NH_3 and HCN, (iv) oxidation of toxic aldehydes, such as HCHO, (v) oxidation of hydrocarbons, such as C_2H_4, and (vi) oxidation of toxic sulfur oxides, such as SO_2 [4-6]. Furthermore, A state-of-the-art BenchCAT reactor was be used for the experimental investigation of CO and C_2H_4 oxidation experiments on Pt/Al_2O_3 powder and monolith scale DOC catalysts. Catalyst activity for oxidation of various toxic components was measured as a function of operating conditions, such as temperature, flow rate, and inlet composition. The experimental data was used to rigorously validate the microkinetic model and to probe the ability of the reaction mechanism to capture the interactions among various species during emissions oxidation.

The detailed reaction mechanism development is carried out using various parameter estimation techniques, such as semi-empirical Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method [7], Transition State Theory (TST), and quantum mechanical Density Functional Theory (DFT). The microkinetic model performs well against various experiments conducted in practically relevant conditions (atmospheric pressure, ppm level concentrations of emission components) and in fixed bed and monoliths reactors. The elementary-step surface reaction mechanism could be utilized for improved design and control of the aftertreatment system as well as appropriate DOC sizing.

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