Development of evaluation test for soot oxidation catalysts

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Introduction

Formulating improved heterogeneous catalysts for soot oxidation is an important aspect to meeting the increasingly stringent emissions regulations for automotive combustion engines. Developing a means of screening potential catalysts for soot oxidation relatively quickly would be useful in this regard. One such tool is simultaneous thermal analysis (STA) which includes both TGA (thermal gravimetric analysis) and DTA (differential thermal analysis) components. Summarized here is the initial work conducted at MEL Chemicals Inc. in developing STA as a tool for evaluating the efficacy of catalysts for the oxidation of soot.

Materials and Methods

For the work presented here, carbon black was used a surrogate for soot. One carbon black was chosen for all the tests – Raven 1080 (Columbia Chemical Company), referred to here on simply as "carbon black". Similarly, a single mixed oxide catalyst prepared at MEL Chemicals Inc., referred to here on simply as "catalyst", was used for all experiments.

Several different mixtures of catalyst and carbon black with specific catalyst to carbon black mass ratios were made by mixing known amounts of each component in a disposable plastic sample cup so that the total mass of each mixture was between 0.1 and 0.2 g.

A 1mg to 30mg aliquot of a specific catalyst/carbon black mixture was then placed in a Pt TGA/DTA pan and placed in the TGA/DTA instrument (Rheometric Scientific STA 1500). The instrument was programmed to have the temperature increase at a rate of 10°C/min from ambient temperature to ~750°C. The data was transferred to an Excel spreadsheet and the raw ΔT data normalized by subtracting a background scan then dividing each data point by the mass of carbon black contained in the TGA/DTA pan.

Results and Discussion

Tests in which the catalyst-to-carbon black ratio was held constant (at ~2.0) but which the amount of material being tested was varied yielded ΔT (DTA) vs. temperature plots whose shape varied systematically but which the onset temperature was constant at 496±7°C.

Reviewing the DTA onset temperature, which we can use as an indication of the exotherm position, for tests in which the catalyst-to-carbon black ratio was deliberately varied, it is observed that the exotherm temperature systematically decreases with increasing catalyst-to-carbon black ratio. For catalyst-to-carbon black ratios of 0.0 (pure carbon black), 2.0, 5.8, 8.0, and 13.3 the corresponding exotherm temperatures are 559, 497, 480, 449, and 451°C.

From the TGA data, the mass of carbon black oxidized vs. temperature can be determined. See **Figure 1**. Note the near linear regions between about 590°C and 660°C. Assuming the rate of carbon oxidation follows a classical rate law, preliminary modeling of these data suggests that only the amount of catalyst present controls the observed rate.

Plotting the ΔT data, normalized with respect to the carbon black oxidized, at a particular point in the experiment versus reaction progress - defined here as the percentage of the carbon black oxidized at that point with respect to the total carbon black ultimately oxidized – reveals possible differences in reaction mechanism based on differences in the shape of the curves. See **Figure 2**, above.

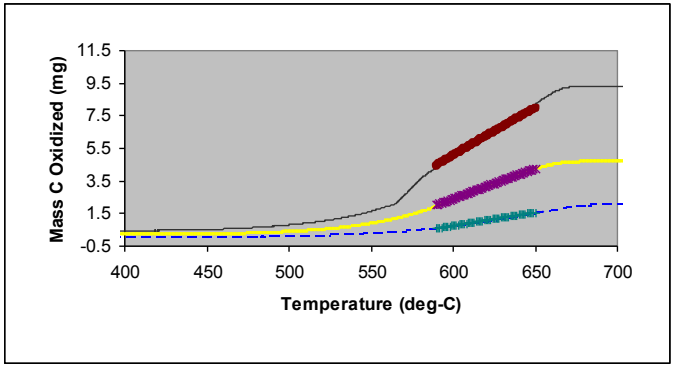

Figure 1. Mass of carbon oxidized vs. temperature for a constant catalyst-to-carbon black ratio (~2.0) but different amounts of material used: 27.9 mg (upper curve), 15.2 mg (middle curve), and 6.0 mg (bottom, dashed curve). For clarity, only the results from three experiments are shown. Modeling results are shown as points.

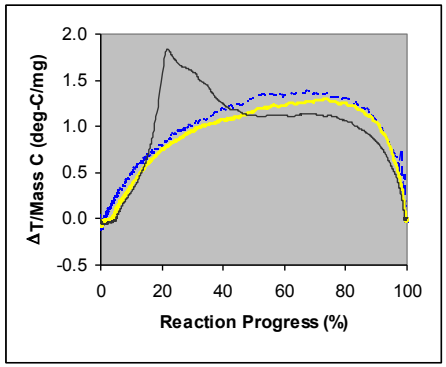

Figure 2. Plot of ΔT (DTA) per mg of carbon black oxidized (TGA) vs. reaction progress for different amounts of material: 27.9 mg (solid curve with strong ΔT peak), 9.9 mg (light-colored curve), and 6.0 mg (dashed curve). Again, only the results from three experiments are shown for clarity. Note that the 27.9 mg data shows significant deviation from the rest, possibly indicating a change in reaction mechanism.

Significance

Some of the results from initial test development work based on simultaneous thermal analysis have been presented here. The full analyses of the DTA and TGA data (both data presented here and additional data) from a suite of experiments will demonstrate the utility of this technique in establishing potential metrics for evaluating and screening materials for use in soot oxidation applications.