High Capacity Sulfur Dioxide Absorbents For Diesel Engine Emissions Control
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Introduction
The emission of particulates and NOx from on-road diesel trucks is an important environmental problem. The EPA has mandated a 95% decrease in their production by 2010 relative to current standards [1]. Major efforts are underway to reduce these emissions through the implementation of particulate filters and regenerable NOx traps [2]. Sulfur oxides (primarily SO2) that are present in the diesel exhaust will gradually decrease the effectiveness of NOx traps [3,4]. SO2 is oxidized to SO3 over the NOx trap catalyst, and SO3 reacts to form sulfates. These sulfates are not fully removed during the rich gas regeneration period that converts adsorbed nitrates to N2, leading to the need for a high temperature desulfation step. This results in a gradual degradation of the NOx trap over the course of many cycles.

An approach to improving NOx trap longevity is to develop a high capacity sulfur oxide-specific trap that is located upstream and can be replaced at regular intervals during engine maintenance. We have identified a promising class of SO2 absorbents based on manganese oxide octahedral molecular sieves (OMS). These materials comprise MnO6 octahedra that are assembled to share faces and edges, resulting in a family of porous absorbents differentiated by the number of octahedra on a side. This paper focuses on the SO2 and SO3 absorption properties of these materials, especially the 2x2 structure cryptomelane, which was measured to have the highest capacity and fastest absorption kinetics toward SO2.

Experimental
Cryptomelane was prepared using the methods developed by DeGuzman, et al [5]. A typical synthesis (reflux method) was carried out as follows: 11.78 g (74 mmoles) KMnO4 in 200 mL of water was added to a solution of 23.2 g MnSO4·4H2O (104 mmoles) in 60 mL of water and 6 mL of concentrated HNO3. The solution was refluxed at 100°C for 24 hr, and the product was washed and dried at 120°C. The yield was 18.3 g.

The test setup employed a small fixed bed reactor (quartz tube, 3.9 mm i.d.), which was heated by a small clam-shell furnace. Typical measurements employed a 0.5 g sample, sieved to 40-80 mesh. Reactant gases were metered using mass flow controllers. The analytical system comprised a HP6890 gas chromatograph equipped with a Sulfur Chemiluminescent Detector (SCD). The analytical system is capable of detecting both SO2 and SO3, and has been described previously [6]. During the experimental run the analytical system operated continuously, sampling the effluent every two minutes. The accuracy of the system at maximum sensitivity of the system to SO2 (with SO2 feed levels 10 ppm) is approximately ±100 ppb, and to SO3 (with 250 ppm SO2 feed) is approximately ±3 ppm.

Results and Discussion
Figure 1 shows the result of SO2 absorption by cryptomelane at 325°C, using 250 ppm SO2 in air as feed gas at a GHSV of 8000 h⁻¹. Two different traces are shown. One plots the ratio sulfur out/sulfur in, and provides a ready visualization of the SO2 breakthrough point at 59%. The breakthrough capacity was defined as the point where SO2 out exceeded 1% of SO2 in. The other trace is a plot showing cumulative and total capacity as a function of SO2 fed to the absorber. The total capacity (71%) was defined as the point beyond which SO2 out exceeded 90% of SO2 in. Once breakthrough occurred, the amount of SO2 at the exit of the bed increased fairly rapidly.

Figure 1: SO2 absorption by cryptomelane K2MnO4 at 325°C

The effect of absorption temperature, flow rate (space velocity), SO2 concentration, and feed gas composition will be described. In the absence of oxygen, cryptomelane is a stoichiometric oxidant that produces SO3 from SO2 and stores the SO3 as MnSO4. However, with oxygen present in the feed gas, cryptomelane displays redox activity. SO2 capacity does not decrease in the presence of CO and NO, which are oxidized to CO2 and NO2 respectively but are not absorbed as either carbonates or nitrates on the cryptomelane absorbent.

References