CATALYTIC OXIDATION FOR ELIMINATION OF METHYL BROMIDE FUMIGATION EMISSIONS

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Abstract. The goal of this project is to design a catalytic system for the elimination of atmospheric emissions of methyl bromide. The experimental setup and preliminary results of catalytic destruction are presented.

Catalytic destruction. An efficient method for destroying volatile organic compounds (VOCs) is incineration in which the compound is oxidized by molecular oxygen. The temperature of oxidation can be greatly lowered by employing suitable nano-structured catalysts. Catalysts used in oxidation of VOCs fall into two major categories: supported transition metal oxides and supported noble metals. A major operational limitation for such nano-structured catalysts is the tendency for the active metal to sinter into its corresponding bulk material. To improve sinter-resistance and catalyst regenerability, “core-shell” catalysts with metal-oxide shells covering the metal core have been recently designed. The shell coating is either a chemically-inert support (e.g. SiO_2) or a support that also serves to augment catalytic activity (e.g. CeO_2).

Preparation of catalysts. The catalysts we have synthesized include two groups:
(1) Nanoscale core-shell spherical particles, M@SiO_2 or M@CeO_2/Al_2O_3, where M is Pt or Pd. Palladium is reported to be more active than other metals for short-chain hydrocarbons oxidation. Platinum is one of the major active components in combustion applications. These two metals outperform other metals as catalysts due to their high ability to activate H_2, O_2, C-H, and O-H bonds. We have already synthesized Pd@SiO_2, in which a mixture of tetraethyl orthosilicate and *n*-octadecyl trimethoxysilane was employed as the SiO_2 precursor, and hydrazine was used as reducing agent. For comparison purposes, control samples of Pd supported on silica spheres, Pd/SiO_2, have also been prepared by a wet impregnation method. The loading of Pd for both cases was about 6%.

(2) Supported noble metals or transition metal oxides on mixed oxides: M/CeO_2-Al_2O_3, M/TiO_2, where M is Pt or Pd; PbO, Fe_2O_3 and CoO/TiO_2. Alumina has been widely and efficiently used for the oxidation of VOCs due to its relative large surface area and low cost. Titania has been reported to be less susceptible to bromide poisoning. Ceria can store and release lattice oxygen to promote catalyst activity and stability. Destruction mechanisms for saturated halogenated VOCs were found to depend on catalyst support in some cases. The support effects will, therefore, be tested.

Experimental setup. The evaluation of catalysts is conducted using a continuous fixed-bed quartz reactor (Figure 1). A constant flow of 64 mgL^{-1} methyl bromide, a level that might be encountered at the end of a chamber fumigation event, was conveyed through stainless steel coil tubing to the reactor. Condensation of methyl bromide in the tubing was prevented by heating the gas cylinder in a water bath to 38^{o}C. The on-line measurement of the methyl bromide in the effluent gases from the reactor is measured by gas chromatography on an Agilent 6890 GC equipped with a 6-port gas sampling valve with a 250 μL sample loop and a flame ionization detector (FID). The gas samples were injected by the splitless technique onto an Agilent GS-Q PLOT column (30 m × 0.535 mm) with 20 mL min^{-1} carrier gas (hydrogen) flow rate, 150°C injection port temperature, 100^{o}C oven temperature, and 300^{o}C detector temperature.

Catalyst performance test. The preliminary results of catalyst performance indicated that Pt/CeO_2-Al_2O_3 and Pd/CeO_2-Al_2O_3 nanocatalysts prepared by wet impregnation method showed > 92 % and > 97 % conversion of methyl bromide, respectively, at 300^{o}C. The catalyst showed reusability for at least three runs.

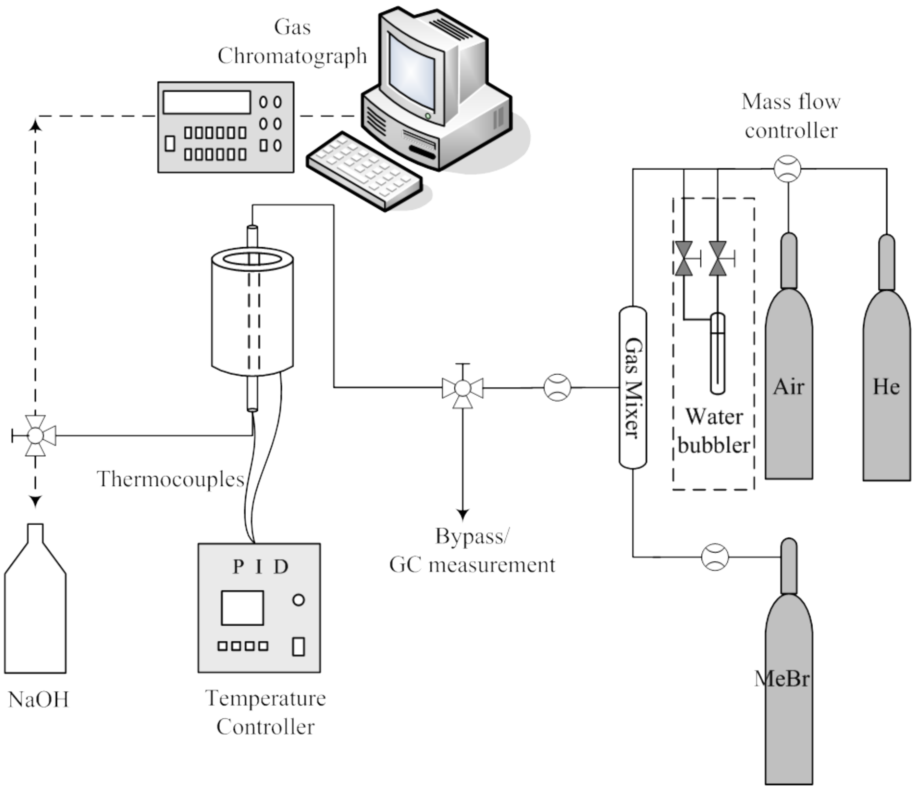

Fig.1. Experimental setup for testing catalytic performance