



Evaluation of platinum catalysts for naval submarine pollution control



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ABSTRACT

Catalytic air purification systems are required to maintain desirable levels of contaminants in confined space pollution control applications, such as onboard naval submarines. These systems execute oxygen generation, CO₂ removal, and burning of contaminants such as carbon monoxide (CO), and hydrocarbons. Crucial characteristics of the catalytic burners on submarines include high activity toward CO combustion, long-term stability in humid environments, and minimal activity towards the decomposition of trace halogenated compounds (often used as refrigerants) that can form toxic acid gas compounds. Here, we compare currently used hopcalite/LiOH catalysts to platinum (Pt) based catalysts deposited on Al₂O₃ and CeO₂ supports for CO combustion, tolerance to humid environments and combustion of model refrigerant contaminant molecules, freon 134a and methyl chloride. The three catalysts exhibit complete combustion of CO in dry air streams by 110 °C, and no catalyst was found to activate freon 134a up to 400 °C. Pt/Al₂O₃ and Pt/CeO₂ catalysts outperformed hopcalite/LiOH by showing enhanced CO oxidation reactivity in the presence of humidity (hopcalite/LiOH is strongly deactivated when H₂O is co-fed), and they are minimally active towards methyl chloride oxidation up to 275 °C, whereas hopcalite/LiOH is active below 200 °C. Pt/CeO₂ exhibited higher reactivity for CO oxidation and lower activity for methyl chloride oxidation, as compared to Pt/Al₂O₃. The results strongly suggest that Pt based catalysts, similar to those used in automotive catalysis, may be excellent replacements for currently utilized hopcalite/LiOH catalysts in naval submarine pollution control applications.

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1. Introduction

Heterogeneous catalysts play a critical role in pollution control applications such as automotive catalytic converters, and the removal of contaminants in confined spaces [1]. Confined space pollution control is a critical component of life support systems on board closed-system manned vessels such as submarines, spacecraft, and mining operations [2,3]. These pollution control systems execute oxygen generation, CO₂ removal, and contaminant combustion, such as carbon monoxide (CO), hydrogen (H₂) and hydrocarbons, as they are generated [4]. On submarines, the air

quality must be continuously maintained within safety standards by the constant removal of trace contaminants to enable extended dive times. Poor air quality control and the resulting necessity to vent the atmosphere can negatively impact tactical advantage in long-term missions.

One of the main air contaminants on board nuclear submarines that must be removed by active confined space pollution control systems is CO [4]. A common catalyst used in pollution control units (CO/H₂ burners) on board nuclear submarines is hopcalite, which is a mixture of copper oxide and manganese dioxide, (CuMn₂O₄, typically ~60% manganese dioxide, and 15–40% copper oxide) [5]. This catalyst has been used for the removal of CO in gas streams over the last century, and has been well characterized [6–12]. Hopcalite catalysts are active for CO removal from room temperature up to 400 °C, but dry gas streams must be used due to the well-known deactivation of hopcalite catalysts in the presence of humidity [12–17]. Higher operating temperatures must be used if humidity is present in the feed stream, which can increase operating

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costs, result in decreased catalyst lifetimes, and drive the activation of halogenated air contaminant compounds, which are typically used as refrigerants [14]. Trace amounts of hydrochlorofluorocarbons (HCFCs) such as Freon 134a (1,1,1,2-tetrafluoroethane; freon herein) and methyl chloride (CH_3Cl ; MeCl herein) can be present in submarine atmospheres, due to the use of refrigerants, at concentrations below harmful levels. However, when circulated through catalytic CO/H_2 burners with the ship air at elevated temperatures, these HCFCs can combust to form dangerous acid gases, such as phosgene and hydrofluoric acid, as was observed in the first patrol of the nuclear submarine USS Tecumseh [2]. To address this problem, adsorbent materials such as LiOH are used to remove the produced toxic acid gases, and prevent further contamination of the atmosphere. The requirement of LiOH adsorbent units to remove acid gases produced from HCFC combustion increases the pollution control system space utilization, which is undesired.

Ideal characteristics of the catalytic combustion systems for confined space pollution control on board submarines include high activity towards CO , H_2 , and hydrocarbon oxidation, long-term stability in humid environments, and no activity towards HCFC oxidation under typical operating conditions. It is clear from many years of work in automotive catalysis that precious metal catalysts provide excellent reactivity, thermal stability, and poison tolerance for CO and hydrocarbon oxidation under a wide range of operating conditions [17–19]. An important active component of automotive catalysis, dispersed Platinum (Pt) nanoparticles on oxide supports, also show promise for low temperature CO oxidation with high tolerance to humid environments [20–24]. However, there have been few comparative studies of Pt-based and hopcalite catalysts for confined space Naval pollution control applications [16,17,19], and none explore the impact of humidity, fluorinated and chlorinated hydrocarbons and metal oxide support composition.

Here, we compare hopcalite/LiOH catalysts with Pt-based catalysts supported on Al_2O_3 and CeO_2 supports for combustion of CO in dry and humid air streams, and oxidation reactivity towards model HCFC compounds (Freon 134a and MeCl). Pt-based catalysts exhibited better performance for confined space pollution control systems in almost all metrics, as compared to hopcalite/LiOH. Pt-based catalysts exhibit complete CO removal above $\sim 100^\circ\text{C}$, no activity for freon activation up to 400°C , strong water tolerance, and minimal MeCl activation until $>300^\circ\text{C}$. Furthermore, the CeO_2 supported Pt uniquely promotes CO oxidation rates at lower temperatures than Al_2O_3 supported Pt, but remains more passive for MeCl oxidation at higher temperatures compared to Al_2O_3 supported Pt. The results strongly suggest that automotive type catalysts that exploit Pt deposited on dispersed CeO_2 on thermally stable Al_2O_3 supports may be an excellent replacement for currently utilized hopcalite/LiOH catalysts in confined space pollution control applications.

2. Methods

2.1. Catalyst synthesis

Colloidal Pt particles were synthesized following an adapted procedure as described previously [25]. In a round bottom flask, 0.25 mL hexachloroplatinic acid solution (Sigma Aldrich, 8 wt.% in H_2O , 0.205 M) and 0.2298 g polyvinylpyrrolidone (PVP; Sigma Aldrich, 55,000 g/mol) was mixed with 5.0 mL of ethanol and 5.0 mL of deionized water. The solution was heated to 100°C and refluxed for 3 h while stirring at 1000 RPM. After cooling to room temperature, the Pt ink solution was prepared for slurry impregnation onto $\gamma\text{-Al}_2\text{O}_3$ and CeO_2 supports at a weight loading of 0.5% Pt (Pt/ Al_2O_3 and Pt/ CeO_2 henceforth). The pH of the ink solution was adjusted to 6 using a 0.05 M NaOH, and the appropriate amount of support

material (~ 2.0 g of total catalyst) was added to the Pt nanoparticle solution and stirred for 14 h in ambient conditions. The solution was washed via centrifugation once with a 0.1 M NH_4NO_3 solution and three times with deionized H_2O . The resulting catalyst was transferred to an evaporation dish to dry overnight in a vacuum oven ($100\text{--}110^\circ\text{C}$). After drying, the samples were sieved (120 mesh) and calcined (500°C) for 5 h. Carulite 300 (hopcalite with no LiOH), and hopcalite/LiOH (Carus Corporation) were used as received. In this report, Al_2O_3 and CeO_2 supports were chosen for direct comparisons with the supports used in monolithic catalytic converters. Al_2O_3 was chosen because it is known to be thermally stable under harsh conditions and to bond reasonably strongly with Pt and therefore maintain a high degree of dispersion. CeO_2 was chosen as it is known to significantly enhance the oxidation reactivity of Pt. These are both common supports used in the automotive industry for related catalytic reactions.

2.2. Reactor studies

Experiments were conducted in a temperature controlled quartz packed bed reactor, where the effluent gas concentrations were measured with online mass spectrometry (HALO 201, Hiden Analytical Inc.). Catalysts were sieved to $<75\ \mu\text{m}$ and diluted 10:1 with inert silica gel (Sigma Aldrich, high purity grade 150 Å) in order to prevent the influence of local heating and internal or external mass transfer limitations during low temperature experiments ($<150^\circ\text{C}$) [26,27]. 50 mg of Pt/ CeO_2 and Pt/ Al_2O_3 and 100 mg of hopcalite/LiOH were used in all experiments. In this report, a larger mass of hopcalite/LiOH catalyst was utilized to account for strong deactivation observed in the presence of water in the reactant stream.

Pt/ Al_2O_3 and Pt/ CeO_2 catalysts were pretreated *in-situ* by heating to 230°C and reducing in H_2 (99.999%, Airgas) for 60 min. The reactor was flushed with He (99.999%, Airgas) and cooled to 200°C , where the catalyst was exposed to CO oxidation reaction conditions (100 ppm CO , 20% O_2 , 10% Ar and balance He) for 6 h. The Pt catalysts were then cooled to 30°C , where a temperature ramp from 30°C to 150°C , holding every 10°C 30 min, was performed to verify that the catalytic activity was consistent with previous measurements. Hopcalite/LiOH samples were heated to 230°C and calcined *in-situ* in O_2 (99.999%, Airgas) for 60 min [10]. The reactor was flushed with He, cooled to 200°C , and exposed to reaction conditions. All further experiments with H_2O , Freon, and MeCl contaminants were performed using identical protocols.

For the exposure and low temperature ($<150^\circ\text{C}$) CO oxidation experiments performed in a humid environment, the temperature at which each catalyst exhibited $\sim 30\text{--}80\%$ conversion (hopcalite/LiOH = 50°C , Pt/ CeO_2 = 65°C , Pt/ Al_2O_3 = 95°C) was held while 70% of the reactant flow was diverted through a water bubbler at 25°C prior to delivery to the reactor, which resulted in $\sim 2\%$ H_2O in the reactant gas stream prior to the catalyst bed. The impact of water at a constant temperature was then monitored for at least 60 min or until the catalyst was stable. The catalyst was then cooled to ambient conditions and a $30^\circ\text{C}\text{--}150^\circ\text{C}$ temperature ramp was performed in humid reaction conditions (100 ppm CO , 2% H_2O , 20% O_2 , 10% Ar and balance He).

Freon oxidation experiments were performed using a fresh catalyst (dry pretreatment) and exposing the catalyst to 10 ppm Freon 134a with CO oxidation reaction conditions (10 ppm Freon 134a, 100 ppm CO , 20% O_2 , 20% Ar and balance He) at 200°C for 30 min, followed by a temperature ramp from 200°C to 400°C , holding for 30 min every 25°C . Freon 134a concentrations were calibrated and measured by online mass spectroscopy using m/z of 33 amu. MeCl oxidation experiments were performed identically to the Freon 134a oxidation experiments using 10 ppm MeCl, 100 ppm CO , 20%

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