

PROPANE OXIDATION OVER Pt/SrTiO₃ NANOCUBES

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INTRODUCTION

Liquefied petroleum gas (LPG) is gaining ground as an alternative fuel because of its clean burning ability, high octane rating and produces considerably lower pollutants than gasoline or diesel [1]. However, tailpipe emissions from LPG fueled vehicles still produces up to 80% of the HC emissions in the first 60 to 90 seconds following a cold-start [2]. This is due to the catalytic converter's inability to oxidize HCs at low temperatures (between 200 to 300 °C). The main goal of this work is to develop and characterize low light-off oxidation catalysts in an effort to reduce tailpipe HC emissions.

Platinum is considered as one of the most active materials for HC oxidation and perovskite-based materials have been investigated since the 1970s as promising auto exhaust catalysts to replace the existing noble metal-based catalysts [3]. Few studies have applied perovskite as supports for Pt to enhance the HC oxidation activity at low temperature. This combination may be promising because of the electronic interaction between Pt and the perovskite support. Our group synthesized highly uniform Pt nanoparticles coated over SrTiO₃ nanocubes. The effect of Pt loading on the propane oxidation activities and light-off temperature is reported. Transmission electron micrograph and scanning electron micrograph was utilized to measure the Pt dispersion and study the Pt particle stability.

EXPERIMENTAL

Sol-Precipitation coupled with Hydrothermal Synthesis were the methods used to prepare the SrTiO₃ nanocubes [4]. The catalyst samples were prepared using Atomic layer deposition (ALD) method in which platinum precursor (methylcyclopentadienyl trimethyl platinum) was deposited at 300 °C over SrTiO₃ nanocubes consisting of 1 to 5 Pt deposition cycles. The Pt loading varied linearly with the number of Pt ALD cycles from 4.0 wt% at 1 cycle to 21.5 wt% at 5 cycles.

The propane oxidation light-off experiments were conducted in a ¼" OD quartz U-tube micro-reactor. The reactant mixture consisted of 0.6% C₃H₈ and 10.6% O₂ with Ar as a diluent. The propane weight hourly space velocity (WHSV) was varied from 4 to 500 hr⁻¹ for light-off temperature studies and approximately 10,000 hr⁻¹ for turnover frequency (TOF) measurements. To determine the light-off temperature, the C₃H₈ conversion was measured at room temperature with 25 °C increments up to 400 °C. Afterwards, the catalyst was cooled down to room temperature in reactant gas. A second temperature ramp was then performed for reproducibility. The light-off temperature, T₅₀, is defined as the temperature at which 50% propane conversion is achieved. Propane oxidation TOFs were measured at 250 °C with propane conversion of less than 10%. The only reaction products were carbon dioxide and water.

RESULTS

Platinum-based catalysts are known to be highly active for the deep oxidation of hydrocarbons. However, typical catalysts such as Pt/γ-Al₂O₃ require relatively high temperatures in order to completely oxidize lower alkanes such as ethane or propane. Preliminary results of this work show that Pt/SrTiO₃ has 70°C lower propane oxidation

light-off temperature (Fig 1) and higher propane turn over frequency than the standard Pt/γ-Al₂O₃ catalyst. Pt/SrTiO₃ is a very robust catalyst. It does not need pretreatment prior to catalytic testing. It can also withstand several temperature cycles without exhibiting activity change. The effect of Pt loading and propane to oxygen feed ratios on light-off behavior and propane turnover frequency will also be presented.

Scanning electron micrographs of these catalysts illustrate a highly uniform distribution of Pt particles over the cubic SrTiO₃ (Fig 2). The Pt particles range from 2 to 4 nm in size. Transmission electron micrographs of the spent catalysts will also be reported.

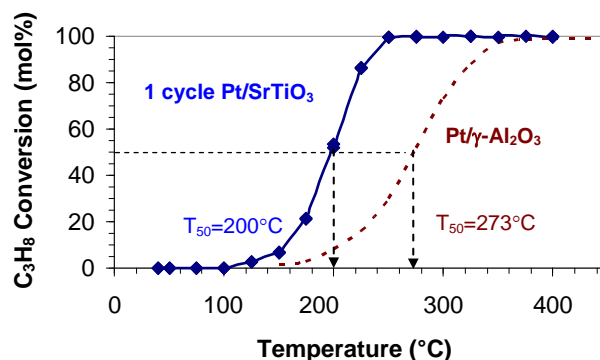


Figure 1: Propane oxidation light-off curve for 3 cycles of Pt/SrTiO₃ and Pt/γ-Al₂O₃ [5]. Propane weight hourly space velocity was 4 hr⁻¹.

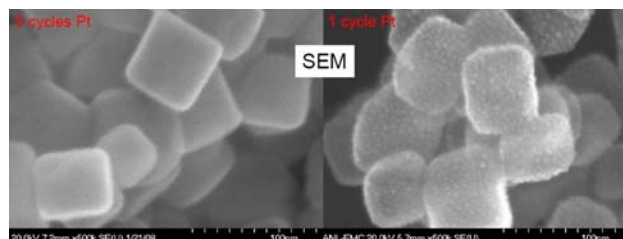


Figure 2: Scanning electron micrographs of SrTiO₃ and 1 cycle Pt ALD/ SrTiO₃.

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