Highly Uniform Platinum Nanoparticles Supported on $SrTiO_3$ Nanocubes for Propane Oxidation

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Introduction

Perovskite-based materials have been investigated since the 1970s as promising auto exhaust catalysts while platinum is considered as one of the most active materials for hydrocarbon (HC) oxidation [1]. Few studies have applied perovskite as supports for Pt to enhance the HC oxidation activity at low temperature. Our group synthesized highly uniform Pt nanoparticles coated over $SrTiO_3$ nanocubes by using Atomic Layer Deposition method (ALD). In-situ X-ray absorption fine-structure (XAFS) was used to determine the mechanism of the Pt nanoparticle formation over $SrTiO_3$. Transmission electron micrograph (TEM) and scanning electron micrograph (SEM) was utilized to measure the size and dispersion of Pt particles before and after propane oxidation studies. The effect of Pt loading on the propane oxidation activities and light-off temperature is reported.

Materials and Methods

Sol-Precipitation coupled with Hydrothermal Synthesis were the methods used to prepare the $SrTiO_3$ nanocubes [2]. The catalyst samples were prepared using ALD method in which methylcyclopentadienyl trimethyl platinum (MeCPPtMe3) was deposited at 300 °C over $SrTiO_3$ nanocubes consisting of 1 to 5 Pt deposition cycles. Air was used to remove the organic ligands from the Pt precursor.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) of the Pt particles were measured during the Pt deposition cycles. In-situ XAFS The measurements were performed on the insertion-device beamline of the Materials Research Collaborative Access Team (MR-CAT) at the Advanced Photon Source, Argonne National Laboratory. SEM images of $SrTiO_3$ were acquired using a Hitachi S4700 with a field emission gun electron beam source operated at 20 kV. TEM and high-resolution electron microscopy (HREM) images of Pt/$SrTiO_3$ were obtained by a JEOL JEM-2100F electron microscope operated at 200 kV.

Propane oxidation light-off studies and turnover frequency measurements were conducted in a quartz micro-reactor. The catalysts were not reduced prior to reaction testing. Propane conversion was measured at room temperature with 25 °C increments up to 400 °C. The reactant mixture consisted of 0.6% C_3H_8 and 10.6% O_2 with balanced Ar. Propane oxidation turnover frequency was measured at 250 °C with WHSV adjusted to provide propane conversion of less than 10%. The only reaction products were carbon dioxide and water.

Results and Discussion

During the ALD of Pt over $SrTiO_3$, Pt loading varied linearly with the number of Pt cycles from 4.0 wt% at 1 cycle to 21.5 wt% at 5 cycles. During the ALD cycle, XANES and EXAFS spectra indicated that MeCPPtMe3 deposited on the support as the original compound at 100°C. At 300°C, the adsorbed MeCPPtMe3 was partially decomposed and oxygen is necessary to completely remove the remainder organic ligands. SEM and TEM of these catalysts illustrate a highly uniform distribution of Pt particles over the cubic $SrTiO_3$ (Fig 1). The Pt particles range from 2 to 5 nm in size.

Platinum-based catalysts are known to be highly active for the deep oxidation of hydrocarbons. However, typical catalysts such as Pt/γ-Al_2O_3 require relatively high temperatures in order to completely oxidize lower alkanes such as ethane or propane. Preliminary results of this work show that Pt/$SrTiO_3$ has 75°C lower propane oxidation light-off temperature than the standard Pt/γ-Al_2O_3 at comparable Pt loadings (Table 1). Pt/$SrTiO_3$ also showed superior propane turn over frequency compared to the standard Pt/γ-Al_2O_3. Pt sintering was observed after the catalytic testing, however this results in negligible deactivation from the T_{50}. Further information is required to quantify the extent of sintering for these new materials.

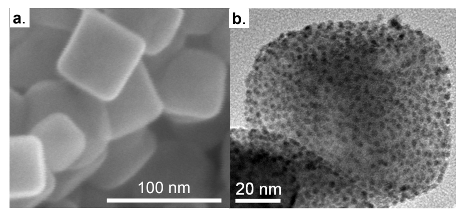

Figure 1. (a) SEM images of as prepared $SrTiO_3$, (b) TEM images of 5 ALD cycles Pt/$SrTiO_3$

Table 1. Propane oxidation turnover frequency at 250°C and light-off temperatures for Pt/$SrTiO_3$ catalysts and Pt/Al_2O_3 references

Sample	TOF (h^{-1})	T_{50} (°C)
1c Pt/$SrTiO_3$	430	198
3c Pt/$SrTiO_3$	1000	185
5c Pt/$SrTiO_3$	2800	168
Pt/Al_2O_3 [3]	-	273
Pt/Al_2O_3 [4]	85	357

Significance

This work demonstrates novel synthesis technique for producing materials with uniform Pt nanoparticles (~ 2-5 nm) and the application of these materials as oxidation catalyst.

References

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