Bowtie-shaped $NiCo_2O_4$ Catalysts for Low-Temperature Methane Combustion

Yiling Dai,[1] PavanKumar Vanama,[1] Chujie Zhu,[2] Haiyan Wang,[2] Kevin J. Smith,[2]* Michael O. Wolf[1]* and Mark J. MacLachlan,[1]*
[1]Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada
[2]Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, British Columbia V6T 1Z3, Canada
* kjs@mail.ubc.ca, mwolf@chem.ubc.ca, mmaclach@chem.ubc.ca

Introduction

Natural gas is a widely available resource that continues to receive tremendous attention as an alternative fuel to gasoline and diesel.[1] NGVs have higher fuel efficiency and lower exhaust emissions (CO, NOx, SOx) than cars that use gasoline or diesel as fuel.[2] However, a significant concern with NGVs is the release of residual unburned methane in the exhaust stream. Thus, the development of new catalysts that can oxidize methane in the exhaust of NGVs continues to be a priority in the transportation sector.

It is not surprising that the quest for effective low temperature methane oxidation catalysts has focused mainly on systems involving precious metals, such as palladium.[3] Although Pd-based catalysts show excellent activity, the high price and low abundance of palladium are limiting factors to practical application. For this reason, the development of alternative catalysts based on non-noble metals is attractive.

Here, we report the preparation of $NiCo_2O_4$ nanostructures with an unusual bowtie shape that show high catalytic activity for low-temperature methane combustion. The growth mechanism of the unusual structures and their catalytic performance were investigated.

Materials and Methods

Bowtie-shaped $NiCo_2O_4$ catalysts were prepared by a hydrothermal method. The precursor was then calcined at elevated temperature to prepare the catalyst. Powder X-ray diffraction (PXRD) analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectra, HRTEM, and tomography studies were performed to investigate the structure of catalysts. Temperature-programmed CH_4 oxidation (TPO) and CO uptake were used to study the catalytic performance.

Results and Discussion

To better understand the origin of the distinctive bowtie morphology observed in the $NiCo_2O_4$ nanocrystals, we systematically varied the synthesis conditions and parameters to see how the changes influenced the structures that emerged. First, the hydrothermal annealing time was varied between 0 and 12 h. The structure of the resulting nickel cobalt hydroxide prepared with different hydrothermal reaction times was examined to understand the growth process. We also investigated the effect of other factors, including metal ratio, capping agents, and presence of oxygen on structure.

The catalytic activity and hydrothermal stability of bow-tie shaped $NiCo_2O_4$ were studied. CO chemisorption experiments were used to titrate the surface metal atoms of the catalysts in order to determine the number of active sites. These experiments reveal that as the calcination temperature is increased, the surface area of the catalyst decreased, resulting in fewer exposed active sites. Turnover frequency (TOF) was calculated based on the active sites. The dependence of TOF on $NiCO_2O_4$ particle size shows that the larger particle size catalysts exhibit higher activity per catalytic site.

Significance

$NiCo_2O_4$ catalysts prepared here exhibit unusual morphology and outstanding catalytic performance among the non-noble metal catalysts, and their catalytic behavior is comparable to some precious metal (Pd)-based catalysts.

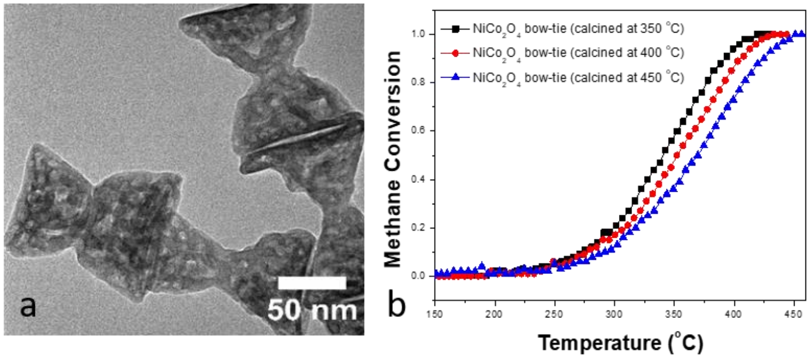

Figure 1. a Bowtie-shaped $NiCo_2O_4$ calcined at 350 °C; b. TPO curves for bowtie-shaped $NiCo_2O_4$ prepared with different calcination temperature. The flow mixture of 1000 ppmv CH_4, 10% (V/V) O_2, balanced by Ar and He, were fed to the reactor at a total flow rate of 150 mL (STP) min^{-1} (space velocity 90,000 mL (STP)$\cdot g^{-1}\cdot h^{-1}$)

References

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