

Reforming Liquid Hydrocarbons with Ni-substituted Barium Hexaaluminates: Effect of Oxygen-conducting Support

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Introduction

Reforming liquid hydrocarbons for solid oxide fuel cell applications requires a thermally stable catalyst with resistance to deactivation in the presence of contaminants at temperatures of 900°C or higher. The use of Ni-based catalysts is attractive because of their low cost relative to precious metal catalysts. However, the liquid hydrocarbon fuels studied for this application contain sulfur and aromatic compounds that poison and deactivate conventional Ni-based supported catalysts, specifically through carbon formation on metal clusters. Deactivation can be minimized by the use of oxygen-conducting supports [1,2] and by substituting active metals into stable oxide structures [3]. However, there are few studies in which active metals have been substituted into thermally stable oxides such as hexaaluminates, and supported on oxygen-conducting materials. Such a catalyst might be expected to have the activity, thermal stability, and resistance to deactivation by carbon deposition necessary for a practical reforming system. The purpose of this study was to compare bulk Ni-substituted barium-hexaaluminate (BNHA) catalyst to this same catalyst supported on an oxygen-conducting material, Gd-doped ceria (GDC), which is intended to minimize carbon deposition in the partial oxidation of a surrogate diesel fuel.

Materials and Methods

Bulk BNHA catalyst was prepared by the co-precipitation method described elsewhere [3]. A 10 wt% layer of BNHA was applied to GDC support via incipient wetness impregnation using nitrate salt precursors dissolved in de-ionized water followed by drying and calcination. Catalytic partial oxidation (CPOX) tests of liquid hydrocarbon fuel surrogates were carried out in a laboratory-scale, fixed-bed reactor, described elsewhere [1]; 50ppm sulfur (as dibenzothiophene) and 5wt% 1-methyl naphthalene (MN) were added to *n*-tetradecane (TD) during a 2-hr portion of the tests. Total carbon in the catalyst bed after reaction testing was determined by temperature programmed oxidation (TPO).

Results and Discussion

The performances of a bulk BNHA catalyst and a system comprised of a 10wt% BNHA layer over GDC support are presented in Figure 1. Both catalysts produced H₂ concentrations corresponding to equilibrium values (~21%) in the presence of TD only. However, the bulk BNHA catalyst deactivated to levels measured for a blank reactor [4] within a 2-hr exposure to the liquid fuel containing both sulfur and aromatic species. When the feed was switched back to pure TD, the H₂ production did not recover, indicating irreversible deactivation. By contrast, the 10wt% BNHA/GDC maintained a much higher level of H₂

production during the 2-hr exposure to deactivating contaminants. Further, this catalyst recovered nearly all of its activity within 1-hr of switching the fuel flow back to pure TD.

The improvement of performance in the presence of GDC support is attributed to its oxygen-conducting properties by the reduction in total bed carbon (TBC) measured by TPO. TBC was 1.04g for the bulk catalyst and 0.60g for the GDC supported catalyst. There was also a qualitative difference in the carbon: carbon deposited on the 10wt% BNHA/GDC was much less refractory and therefore oxidized at a lower temperature by TPO.

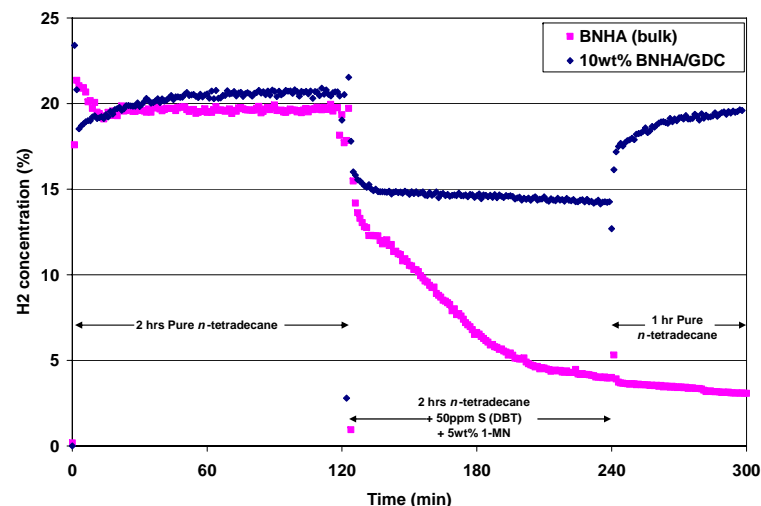


Figure 1. CPOX of TD with bulk BNHA catalyst and BNHA over O₂-conducting support – GDC (Gas Flow = 300sccm; GHSV = 50,000cm³/g-h; O/C = 1.2; P = 20psig; T = 900°C).

Significance

The resistance to deactivation for the Ni-substituted Ba-hexaaluminate is greatly improved by supporting this catalyst on an oxygen-conducting Gd-doped ceria material. This appears to reduce both the quantity and refractory nature of the carbon deposition.

References

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