

Catalytic Partial Oxidation of CH₄ over Ni-Substituted Hexaaluminate Catalysts

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Introduction

The catalytic partial oxidation (CPOx) of methane is an attractive source of H₂ and CO for fuel cell applications. However, the deposition of carbon onto the surface of the catalyst and the migration and loss of active metals remain the principal issues in the development of a suitable catalyst. The formation of elemental carbon onto the surface of a catalyst has been shown to be related to both the size of the active metal cluster [1] and its coordination [2]. The substitution of a catalytic metal into the lattice of hexaaluminate compounds may serve to reduce the size of active metal clusters and to increase their dispersion thereby reducing their susceptibility toward carbon deposition. Interactions between neighboring substituted metals and the hexaaluminate lattice may serve to suppress active metal mobility. In the present work, a series of barium hexaaluminate catalysts with Ni substituted into the lattice were prepared with the general formula, BaNi_yAl_{12-y}O_{19.8} (y = 0.2, 0.4, 0.6, 0.8 and 1.0). The temperature programmed activity and selectivity for this series were investigated.

Materials and Methods

The Ni-substituted barium hexaaluminate catalysts were prepared by co-precipitation from nitrate salt precursors followed by calcination at 1400°C. Prior to the experiments, the hexaaluminate catalysts were first reduced in 5 vol% H₂/Ar at 900°C for 1 hour. Experiments were conducted for the CPOx of CH₄ at an O/C = 1.0, a GHSV = 25,000 cm³h⁻¹g⁻¹, a pressure of 2 atm, a total inlet gas flow rate of 450 sccm and CH₄ and O₂ concentrations of 5.0 and 2.5 vol%, respectively. Catalyst activity and selectivity were examined by temperature programmed reaction of CH₄ over the temperature range 200 to 900°C with a ramp rate of 5°C/min.

Results and Discussion

Figure 1 shows the temperature programmed reaction of CH₄ over the BaNi_{0.8}Al_{11.2}O_{19.8} catalyst compared to non-catalytic reactions occurring over inert quartz chips. Over the temperature range 200 to 400°C, reaction between CH₄ and O₂ was not observed. Between 400 and 665°C the BaNi_{0.8}Al_{11.2}O_{19.8} catalyst exhibited combustion activity with an increase in CH₄ consumption and CO₂ formation. The stoichiometric reaction between CH₄ and O₂ was achieved between 565 and 665°C as indicated by the flat CH₄ and CO₂ concentration profiles. The selectivity towards CO₂ observed over the catalyst in this region suggests that methane oxidation was occurring likely at the leading edge of the catalyst bed [3]. At 665°C, light-off

occurred suggesting that both CH₄ and O₂ were activated on the catalyst surface. All BaNi_yAl_{12-y}O_{19.8} catalysts within the series produced similar catalytic behaviors. Their H₂ production, H₂/CO selectivity and light-off temperatures are given in Table 1. Visual profiling of the catalysts revealed that the upper portion of the bed remained blue and free of carbon and the lower portion achieved a gray appearance suggesting that some carbon formation occurred in the downstream portion of the bed, i.e., after the oxygen was consumed.

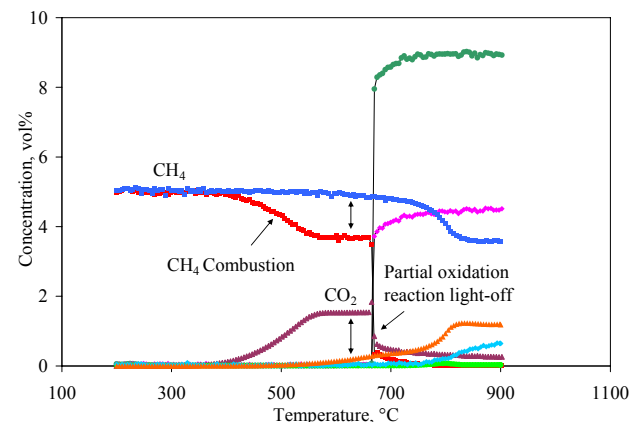


Figure 1. Exit concentrations for the temperature programmed partial oxidation of CH₄ over BaNi_{0.8}Al_{11.2}O_{19.8}: H₂ (●), CO (◆), CO₂ (▲) and CH₄ (■). Exit concentrations for the temperature programmed partial oxidation of CH₄ over quartz: H₂ (●), CO (◆), CO₂ (▲), CH₄ (■).

Table 1. H₂ concentration and H₂/CO selectivity at 800°C and light-off temperatures for BaNi_yAl_{12-y}O_{19.8} catalysts.

	Blank	Equil	y = 0.2	y = 0.4	y = 0.6	y = 0.8	y = 1.0
H ₂ (vol%)	4.1	9.0	9.1	9.0	9.0	9.0	9.0
H ₂ /CO ratio	19.5	2.0	2.0	2.0	2.0	2.0	2.0
Light-off (°C)	-	-	662	665	687	665	665

Significance

Substitution of Ni into the hexaaluminate framework lattice has modified the properties of Ni such that it retains high activity and is less susceptible to deactivation by carbon deposition.

References

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