IV.B.3 Hexaaluminate Reforming Catalyst Development

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Objectives

- The development of a durable, low-cost catalyst to reform middle distillate fuels.
- Evaluate the activity, selectivity and carbon deposition resistance of transition metal doped hexaaluminate-type catalysts:
  - Evaluate the effect of doping the hexaaluminate lattice with noble metals.
  - Perform extended performance test on diesel fuel.

Accomplishments

- Synthesized numerous hexaaluminate and hexametallate catalyst formulations.
- Demonstrated 150 hours of operation on diesel fuel.
- Performed catalyst characterization by X-ray diffraction (XRD), temperature-programmed reduction (TPR), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), temperature-programmed oxidation (TPO) and Brunauer-Emmett-Teller (BET) surface area.
- Evaluated the activity and selectivity of synthesized hexaaluminate samples using methane, n-tetra-decane and diesel fuel.
- Patent disclosure filed for a novel reforming catalyst.

Introduction

The catalytic partial oxidation of diesel fuel is an attractive source of H_2 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 this project, catalytically active metals are doped directly into the hexaaluminate lattice resulting in an atomically dispersed catalyst system that has been shown to possess carbon deposition resistance [3,4].

Recent work sponsored by the National Energy Technology Laboratory has shown progress toward understanding the structure-activity relationship which exists with solid oxide catalysts. Within this study, the average Ni coordination of a $BaNi_yAl_{12-y}O_{19-\delta}$ series of catalysts was characterized by EXAFS. Catalyst activity and selectivity was assessed by H_2 and CO concentrations obtained from methane and n-tetradecane ($C_{14}H_{30}$) partial oxidation. Post-run characterization of the catalysts was undertaken by TPO to locate and quantify the amount of carbon deposited onto the catalysts. The effect of doping the hexaaluminate lattice with noble metals was also evaluated with a 150 hour partial oxidation experiment on diesel fuel.

Approach

The deposition of carbon onto the surface of a reforming catalyst occurs predominately through pyrolytic and dehydrogenation reactions. The dehydrogenation of hydrocarbons into coke occurs when the relative rate of hydrocarbon adsorption is faster than that of the surface reaction [5]. It is therefore desirable to design catalysts which limit the residence time of the hydrocarbon adsorbate to minimize complete dehydrogenation into coke.

The aim of the present study has been to reduce the formation of large ensembles of active sites that are responsible for forming carbon and also for strongly adsorbing sulfur compounds. This was accomplished by substituting catalytically active metals into the framework lattice of hexaalumina. A series of catalysts based on transition metal doped hexaalumina and compounds with hexaalumina-type structure were prepared by co-precipitation from nitrate salt precursors. The stability of one of these catalysts was assessed over 150 hours of continuous operation. Catalyst activity, selectivity and carbon deposition resistance were

investigated over these catalysts utilizing n-tetradecane and diesel fuel.

Results

n-Tetradecane is used in this investigation as a model diesel fuel compound. Within the reactor, oxygen is preferentially consumed at the reactor inlet resulting in the formation of steam and CO_2. These products then react with the n-tetradecane (and its derivatives) in reforming reactions to produce CO and H_2. To illustrate the structure-activity relationship that exists with Ni substituted hexaaluminate catalysts, n-tetradecane catalytic partial oxidation (CPOx) was used as a probe reaction. The results obtained exemplify the effect of increasing the Ni substitution into the hexaaluminate lattice.

Prior to the experiments, the hexaaluminate catalysts were first reduced in 5 vol% H_2/Ar at 900°C for 1 hour. Experiments were conducted at an O/C = 1.2, a gas hourly space velocity (GHSV) = 50,000 $cm^3h^{-1}g^{-1}$, a pressure of 2 atm, a total inlet gas flow rate of 450 sccm and $C_{14}H_{30}$ and O_2 concentrations of 2.17 and 18.22 vol%, respectively. $C_{14}H_{30}$ conversion was observed to be 100%. Catalyst activity and selectivity were examined by isothermal reaction at 900°C. Carbon deposition was measured by TPO using 5% O_2/N_2 and a ramp rate of 1°C/min. The yield of product A (H_2 and CO) is defined as:

Where, N is the number of moles of hydrogen/mole of hydrocarbon for the H_2 yield and is the number of carbon atoms in the hydrocarbon fuel for CO.

$$Yield\ of\ A(\%) = \frac{moles\ of\ A\ in\ reactor\ effluent \times 100}{N \times moles\ of\ hydrocarbon\ fed\ to\ the\ reactor}$$

The EXAFS data for the three catalysts are shown in Table 1. From the data, the average Ni-O bond distance did not vary significantly by increasing the Ni substitution into the lattice, however increasing Ni substitution slightly decreased Ni-O coordination. This suggests that the concentration of Ni present in the lattice remained sufficiently dilute such that these parameters were not significantly affected. The Debye Waller factor was found to be low for all catalysts indicating a well ordered Ni crystalline structure.

TABLE 1. EXAFS Parameters for Ni-O Bonds in $BaNi_yAl_{12-y}O_{19-\delta}$

Catalyst	Avg. Ni-O Coordination	Ni-O Bond Distance (Å)	Debye Waller factor
$BaNi_{0.2}Al_{11.8}O_{19-\delta}$	4.1 ± 0.8	1.935 ± 0.016	0.0020 ± 0.0021
$BaNi_{0.6}Al_{11.4}O_{19-\delta}$	3.0 ± 0.5	1.966 ± 0.008	0.0006 ± 0.0019
$BaNi_{1.0}Al_{11}O_{19-\delta}$	3.0 ± 0.5	1.957 ± 0.013	0.0021 ± 0.0019

The H_2 and CO yields over the $BaNi_yAl_{12-y}O_{19-\delta}$ series of catalysts at 900°C are given in Table 2. The yield indicates that catalyst activity was influenced by the concentration of Ni present. The $BaNi_{0.2}Al_{11.8}O_{19-\delta}$ catalyst exhibited H_2 and CO yields which were 64 and 59% of equilibrium. However, the $BaNi_{0.6}Al_{11.4}O_{19-\delta}$ and $BaNi_{1.0}Al_{11}O_{19-\delta}$ catalysts exhibited near equilibrium H_2 and CO yields. The observed selectivity was significantly lower for the $BaNi_{0.2}Al_{11.8}O_{19-\delta}$ catalyst suggesting that at low Ni substitution the catalyst was not only less active, but also was likely more prone to carbon deposition.

TABLE 2. Product Yields for the CPOx of n-$C_{14}H_{30}$ Over $BaNi_yAl_{12-y}O_{19-\delta}$ at 900°C

Catalyst	H_2 Yield (%)	CO Yield (%)
Equilibrium	89.2	91.5
$BaNi_{0.2}Al_{11.8}O_{19-\delta}$	57.4	54.5
$BaNi_{0.6}Al_{11.4}O_{19-\delta}$	92.7	91.0
$BaNiAl_{11}O_{19-\delta}$	88.3	85.8

The TPO results for the three exposed catalysts are given in Figure 1. The results indicate that increasing the substitution of Ni into the lattice produced distinct differences in both the amount of carbon deposited onto the catalyst and its location. The $BaNi_{0.2}Al_{11.8}O_{19-\delta}$ catalyst exhibited a single asymmetrically shaped burn-off peak located at ~550°C. The asymmetry associated with this peak suggests the presence of two overlapping peaks. The portion of the peak located between 430 and 518°C is, therefore, attributed to carbon located at an interfacial region near, but not on, the Ni surface [6,7]. The portion of the peak located between 518 and 634°C is attributed to carbon located on the support [6,7]. The carbon present on this catalyst is dominated by carbon deposited onto the support. This observation is consistent with a less active catalyst with less Ni metal present on the surface. The relatively high concentration of total carbon deposited onto the catalyst is consistent with the observed poor CO selectivty.

The $BaNi_{0.6}Al_{11.4}O_{19-\delta}$ catalyst exhibited three peaks at various burn-off temperatures. The low temperature peak located at 296°C was attributed to the metal burn-off region [6,7], the peak located at 537°C was identified as carbon located at an interfacial region, and the peak located at 592°C was identified as carbon deposited onto the support [6,7]. A significant decrease in total carbon deposited onto the catalyst was observed at higher Ni substitution. This is consistent with the observed CO selectivity.

The $BaNi_{1.0}Al_{11}O_{19-\delta}$ catalyst exhibited a single broad burn-off peak located at 559°C. The broadness associated with this peak suggests that carbon is located at both interfacial and support regions. This catalyst exhibits the lowest amount of carbon deposited onto the
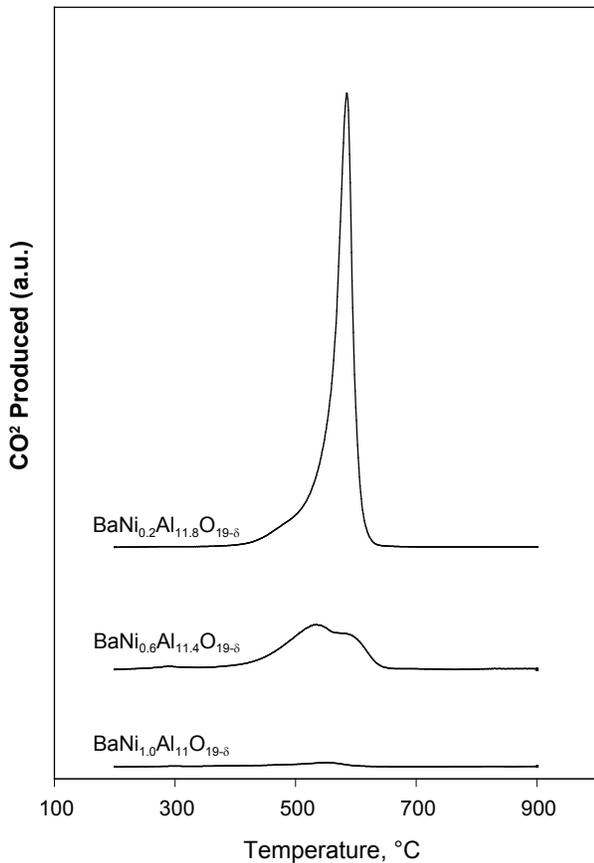
A 150-hour test on diesel fuels was performed on the noble metal doped hexaaluminate catalyst to assess stability as a function of time. Continuous operation of 150 hours on diesel fuel was achieved before the inlet preheat lines clogged with carbon deposits. The diesel fuel compositions examined are given in Table 3. The reaction conditions used were a temperature of 900°C, an O/C = 1.2 and a pressure of 14 psig. The performance results from the experiment are given in Figure 3. From this figure, the catalyst exhibits relatively stable performance on DF #1 for 95 hours. After 95 hours, the fuel was switched to DF #2 for 55 hours where a decline in performance was observed. The change in performance was likely due to the higher concentration of sulfur and aromatic compounds present in DF #2 relative to DF #1. The profile of the reactor contents after the partial oxidation reaction revealed carbon build-up at the leading edge of the bed likely due to dehydrogenation and pyrolysis of inlet feed hydrocarbons.
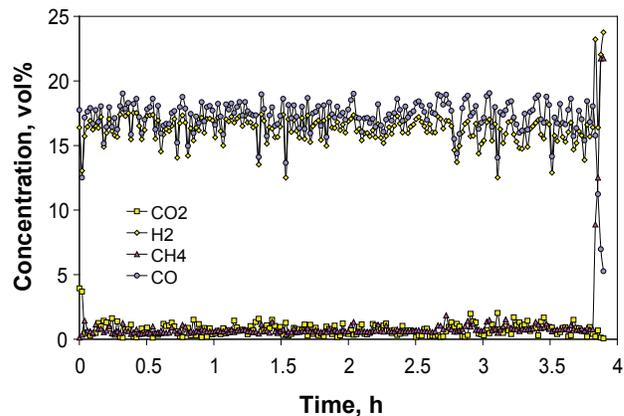

FIGURE 1. TPO Results for $BaNi_yAl_{12-y}O_{19-\delta}$ (y = 0.2, 0.6 and 1.0) Series of Catalysts after the CPOx Experiments with n-Tetradecane

catalyst surface which correlates with the greatest Ni substitution into the lattice.

A performance test run of the NETL-developed fuel atomization/reactor and noble metal doped hexaaluminate catalyst was performed using diesel fuel. The composition of the diesel fuel (DF) is DF #1 given in Table 3. This was the first NETL test to employ both a fuel atomizer and a novel NETL-developed reforming catalyst. The specific test objective was to examine integrated atomizer/catalyst performance and to assess catalyst stability. In this test series, the catalyst was examined at 900°C, at a GHSV = 25,000 $cm^3g^{-1}h^{-1}$, O/C = 1.2. The catalyst exhibited stable performance over the test period (Figure 2).

TABLE 3. Diesel Fuel Compositions

	DF #1	DF #2
Constituent	Concentration (wt%)	Concentration (wt%)
Sulfur	9 ppm w/w	125 ppm w/w
Aromatic	18	23
Paraffin	38	38
Naphthenes	44	39

FIGURE 2. Performance of NETL Fuel Atomizer/Reactor and Noble Metal Doped Hexaaluminate Catalyst
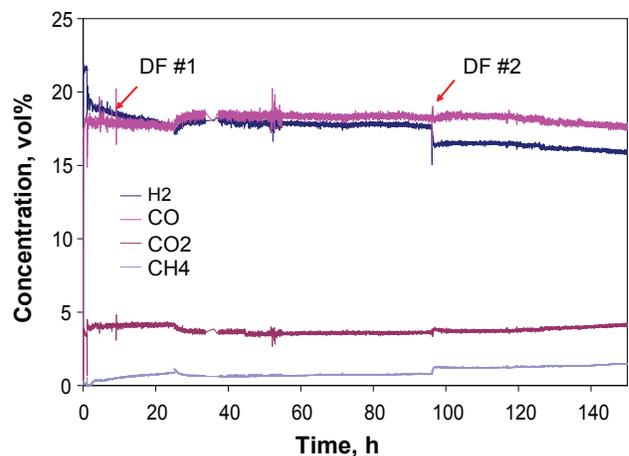

FIGURE 3. 150 Hour Performance Test with Diesel Fuel over a Noble Metal Doped Hexaaluminate Catalyst

Conclusions and Future Directions

EXAFS analysis of the $BaNi_yAl_{12-y}O_{19-\delta}$ catalysts has shown the average Ni-O bond distance to be relatively insensitive to increasing Ni substitution, however increasing Ni substitution decreased Ni-O coordination. Catalyst activity and selectivity was shown to be strongly dependant on the Ni substitution. TPO of the reacted catalysts indicates that carbon deposited onto the surface of the catalysts was directly related to their activity and selectivity. The addition of noble metals to the lattice hexaalumina was effective at producing stability toward deactivation. A 150-hour test with diesel fuel over this catalyst showed good stability.

Future Directions

- Improved catalyst activity and carbon deposition resistance.
- Continue to evaluate the activity and selectivity of platinum group metals doped hexaaluminate catalysts.
- Improved sulfur resistance:
  - Evaluate the effects of high temperature operation on sulfur resistance.

Acknowledgements

EXAFS studies were carried out at LSU's synchrotron facility (Baton Rouge, LA).

Special Recognitions & Awards/Patents Issued

1. "Nano-structured noble metal containing catalysts based on hexametallate architecture for the reforming of hydrocarbon fuels to hydrogen and carbon monoxide and method for making the same," Patent disclosure filed.

FY 2007 Publications/Presentations

1. "Catalytic Partial Oxidation of Hydrocarbon Fuels: Structural Characterization of Ni-Substituted Hexaaluminate Catalysts," *American Chemical Society National Meeting 2007, Division of Fuel Chemistry Preprints,* Boston, MA, August 2007.

2. "Catalytic Partial Oxidation of CH_4 over Ni-Substituted Hexaaluminate Catalysts" *North American Catalysis Society, 20th North American Meeting*, Houston, TX, June 2007.

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