

Partial Oxidation of n-Tetradecane over Lanthanum Ni-Hexaaluminate

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Introduction

The most promising route to hydrogen production from middle distillate fuels is catalytic reforming. For this application, the National Energy Technology Laboratory (NETL) is developing a new class of catalysts based on hexaalumina. Hexaalumina is of interest for this application primarily due to its layered spinel structure that has been shown to be stable at high temperatures [1, 2]. Catalytically active metals are doped directly into the structure resulting in a highly dispersed catalyst system that has been shown to possess reductive and thermal stability [3, 4].

The purpose of this paper is to examine the suitability of hexaaluminate catalysts for high temperature partial oxidation of middle distillate fuels. The partial oxidation reforming characteristics of $\text{LaNiAl}_{11}\text{O}_{19}$ with a model diesel fuel compound, n-tetradecane, were examined. Its thermal stability, reductive resistance and activity were characterized using BET surface area, TPR and micro-reaction studies.

Experimental

$\text{LaNiAl}_{11}\text{O}_{19}$ was prepared by dissolving nitrate salt precursors in deionized water at 60°C. The nitrate salt solution was then added dropwise to a solution containing excess ammonium carbonate at 60°C. The resultant gel was aged for 8 hours at 60°C while maintaining the pH between 7.5 and 8.5. The gel was then filtered and washed to remove excess nitrate and dried for 24 hours at 110°C. The dried filter cake was then crushed and calcined at 1200, 1250 and 1300°C for both 2 and 4 hour indurations.

The reducibility of $\text{LaNiAl}_{11}\text{O}_{19}$ was characterized by temperature programmed reduction (TPR) using an ASAP 2910 (Micromeritics, inc.) Automated Catalyst Characterization System. The detector used was a thermal conductivity detector and the conditions used were 0.2 g of catalyst and 5 vol% H_2/Ar at 50 sccm.

Partial oxidation of n-tetradecane over $\text{LaNiAl}_{11}\text{O}_{19}$ was carried out in a BTRS-jr. (Autoclave Eng.) reaction system. The reaction test cell was a fixed bed with an 8 mm inner diameter made from Incoloy 800HT. The partial oxidation reaction was carried out at 850°C , 197.9 kPa (14 psig), a GHSV of $10,000 \text{ cm}^3\text{h}^{-1}\text{g}^{-1}$, an O/C=1.2 and a total flow of 400 sccm. The exit gases were analyzed continuously by an online 200 amu scanning magnetic sector (ThermoOnix) mass spectrometer.

Results

The $\text{LaNiAl}_{11}\text{O}_{19}$ catalyst was calcined at various times and temperatures to examine the effect of heat treatment on surface area. Table 1 shows that calcination time and temperature both produced a significant effect on surface area. Lower temperature and shorter calcination time resulted in higher surface areas. The temperature change from 1200 to 1250°C produced a greater reduction in surface area than the temperature change from 1250 to 1300°C . Similarly, samples calcined at 1250°C produced a greater reduction in surface area from 2 to 4 hour indurations than did calcination at 1200 and 1300°C .

Table 1. $\text{LaNiAl}_{11}\text{O}_{19}$ surface areas.

Temp. ($^\circ\text{C}$)	Time (h)	N_2 BET Surface Area (m^2/g)
1200	2	12.4
	4	11.7
1250	2	9.9
	4	8.9
1300	2	8.4
	4	7.7

The reduction resistance of $\text{LaNiAl}_{11}\text{O}_{19}$ catalysts was determined by TPR in 5 vol% H_2/Ar . As shown in Figure 1, the TPR profile for $\text{LaNiAl}_{11}\text{O}_{19}$ exhibited a single broad reduction peak starting at 750°C and ending at 1100°C . Nickel has been shown to substitute directly into hexaaluminate as Ni^{2+} [5]. The reduction peak centered at 996°C ; is therefore, indicative of nickel reducing from Ni^{2+} to Ni^0 . Pure NiO is known to have a reduction profile between 300°C and 500°C with a peak centered at 400°C [6, 7]. Substitution of nickel into the hexaaluminate structure, therefore, imparted a high degree of reduction stability.

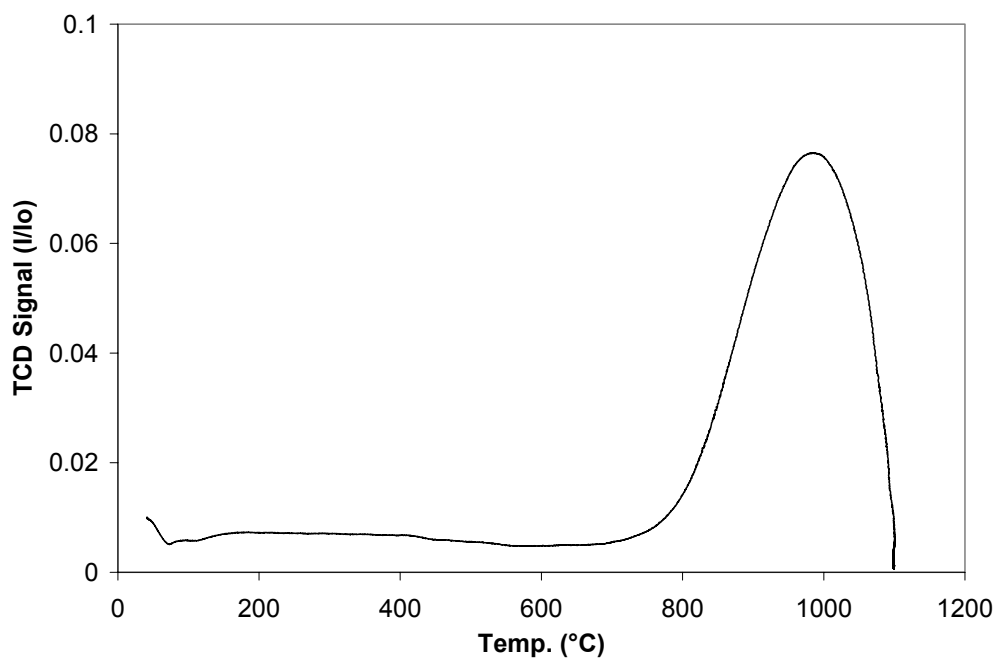


Figure 1. TPR of LaNiAl₁₁O₁₉ catalyst in 5 vol% H₂/Ar.

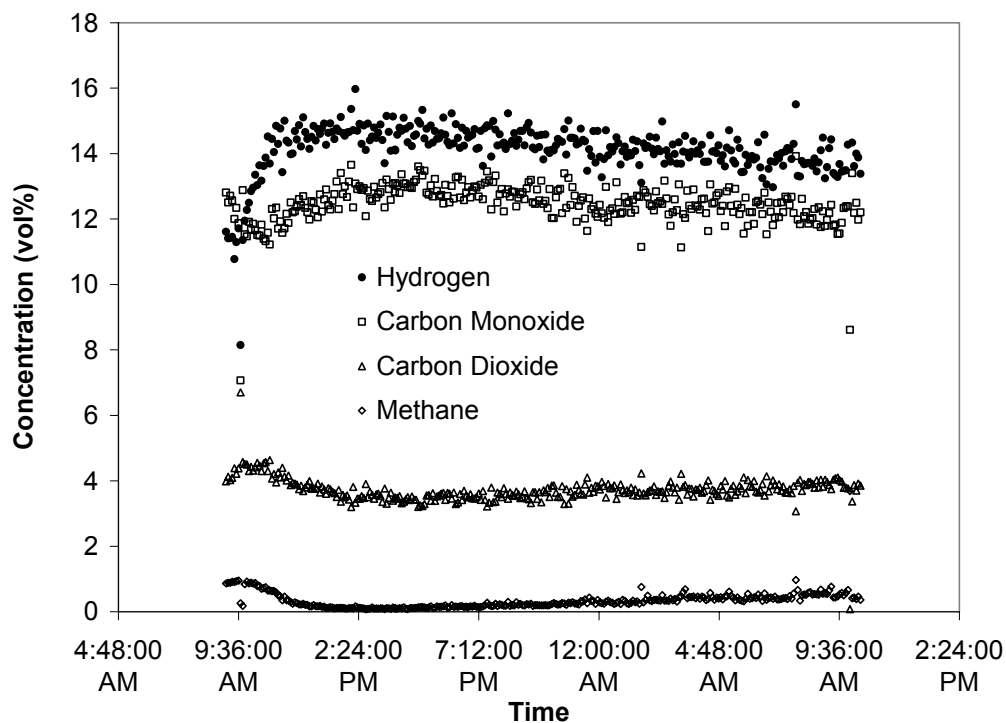


Figure 2. Product composition from n-tetradecane partial oxidation over LaNiAl₁₁O₁₉.

Figure 2 shows the conversion activity and selectivity for n-tetradecane partial oxidation over $\text{LaNiAl}_{11}\text{O}_{19}$, conducted at $\text{O/C} = 1.2$, $T = 850^\circ\text{C}$, $P = 197.9 \text{ kPa}$ and a $\text{GHSV} = 10,000 \text{ cm}^3\text{h}^{-1}\text{g}^{-1}$. The catalyst was first pre-reduced in 5 vol% H_2 at 850°C for 8 hours. The average selectivity toward H_2 was 66.2% and CO was 60%. The H_2/CO ratio remained constant over 24 hours of operation at 1.18. Table 2 provides a comparison of equilibrium product values to average product composition values obtained from n-tetradecane partial oxidation.

Table 2. Equilibrium concentration of n-tetradecane partial oxidation at 850°C , 197.9 kPa , $\text{O/C}=1.2$.

Component	Equilibrium concentration (dry basis) (vol%)	Concentration (dry basis) (vol%)
N_2	67.6	68.5
H_2	15.9	14.9
CO	15.0	12.6
CO_2	1.53	3.75
CH_4	0.019	0.220

Conclusions

Nickel substituted lanthanum hexaaluminate exhibited relatively high surface areas, between 12.4 and $7.7 \text{ m}^2/\text{g}$, with calcinations temperatures between 1200 and 1300°C . This material also exhibited a high degree of reductive stability as determined by TPR with a peak temperature of 996°C . n-Tetradecane partial oxidation experiments indicated that this catalyst is very active for partial oxidation and exhibits a high selectivity toward H_2 and CO .

References

1. Machida, M., Shiomitsu, T. and Eguchi, K., *J. Solid State Chem.* 95 (1991) 220-223
2. Machida, M., Eguchi, K. and Arai, H., *J. Catal.* 103 (1987) 385-393
3. Xu, Z., Zhen, M., Bi, Y. and Zhen, K., *Catal. Lett.* 64 (2000) 157-161
4. Xu, Z., Zhen, M., Bi, Y. and Zhen, K., *Appl. Catal. A: Gen.* 198 (2000) 267-273
5. Xu, Z., Zhen, M., Bi, Y. and Zhen, K., *Catal. Lett.* 64 (2000) 157-161
6. Rynkowski, J. M., Paryjczak, T. and Lenik, M., *Appl. Catal. A.* 106 (1993) 73
7. Chu, W., Yang, W. and Lin, L., *Catal. Lett.* 74 (2001) 139-144