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Catalytic oxidation of methane over hexaaluminates and hexaaluminate-supported Pd catalysts

Ben W.-L. Jang[a,*], R.M. Nelson[a], James J. Spivey[a], Meltem Ocal[b], R. Oukaci[b], George Marcelin[b]

[a]*Center for Engineering and Environmental Technology, Research Triangle Institute, PO Box 12194, Research Triangle Park, NC 27709-2194, USA*

[b]*Department of Chemical Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261, USA*

Abstract

An aqueous $(NH_4)_2CO_3$ coprecipitation method, based on that of Groppi et al. [Appl. Catal. A 104 (1993) 101–108] was used to synthesize $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ hexaaluminates. These materials were first synthesized by alkoxide hydrolysis. This synthesis route requires special handling of the starting materials and is not likely to be commercially practical. The materials prepared by $(NH_4)_2CO_3$ coprecipitation have similar surface areas as those prepared by the alkoxide hydrolysis method. Their CH_4 oxidation activity, measured as the temperature needed for 10% conversion of methane, is higher than those prepared by alkoxide hydrolysis. The La-substantiated material, $LaMnAl_{11}O_{19-\alpha}$, shows high surface area with 19.3 m^2/g after calcination at 1400°C for 2 h. It is active for CH_4 oxidation with $T_{10\%}$ at 450°C using 1% CH_4 in air and 70 000 cm^3/h g space velocity. The stability and activity of $LaMnAl_{11}O_{19-\alpha}$ prepared by $(NH_4)_2CO_3$ coprecipitation method is a simple and important step forward for the application of CH_4 catalytic combustion for gas turbines.

Keywords: Hexaaluminates; Catalytic combustion; Natural gas; Catalyst synthesis

1. Introduction

Catalytic combustion of natural gas is a promising technology for energy conversion processes because it minimizes the emissions of NO_x, CO, and hydrocarbons [2–6]. Although it has been proposed for many industrial applications, such as gas turbines, boilers, and jet engines, the major difficulty is to develop a practical catalyst and support that has both high-temperature stability and low-temperature activity [2–6].

Various heat-resistant metal oxides have been tested as catalysts and supports for catalytic combustion of CH_4, e.g., perovskites [7–10], Co_3O_4 [7], spinels [11], etc. Recently, hexaaluminate catalysts have been reported to have high activity for methane combustion and promising thermal stability [1,12,13]. Among all the catalysts, Ba–Mn and Sr–La–Mn hexaaluminates were the most thermally stable and active in several studies [1,12,13]. Before the report by Groppi et al. [1], an alkoxide hydrolysis method was used for the synthesis of high surface hexaaluminates [12–15]. This preparation has to be carried out under an oxygen and moisture-free environment, which is industrially impractical. A key development is the aqueous copre-

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*Corresponding author.

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cipitation technique with $(NH_4)_2CO_3$ used to prepare some of these catalysts. Groppi et al. [1] used an aqueous solution in excess $(NH_4)_2CO_3$ to synthesize Ba–Mn hexaaluminates and showed that these catalysts have surface areas and CH_4 oxidation activity that are comparable to those prepared by the alkoxide hydrolysis method. This is important because, if there is commercial interest in these materials, they must be manufactured in a simple way.

Arial and his coworkers [5,12–14] reported that various cations can be substituted into the hexaaluminate structure. However, replacing one Al atom with Cr, Ni or Co in $BaAl_{12}O_{19}$ did not improve the CH_4 oxidation activity, although high surface area was maintained. On the other hand, replacing one Al by Fe or Mn greatly increased the methane oxidation activity [12]. $BaMnAl_{11}O_{19-\alpha}$ was the most active of the Ba–M hexaaluminates for CH_4 oxidation. Further replacing Ba of $BaMnAl_{11}O_{19-\alpha}$ with K, Sr, La, or Ca also changes the CH_4 oxidation activity with the Sr–La–Mn hexaaluminate being the most stable and active catalyst for CH_4 oxidation [13].

Although Pd-based catalysts are known to be most active for CH_4 oxidation [16–19], these catalysts lose activity at high temperatures when PdO decomposes to Pd. The focus of this study is to investigate the synthesis and catalytic oxidation activity of various hexaaluminates prepared by aqueous $(NH_4)CO_3$ and NH_4OH precipitation methods because NH_4OH is a common alternative base for precipitation. The activity and stability of Sr–La–Mn hexaaluminate for CH_4 oxidation and as support materials for Pd was investigated.

2. Experimental

2.1. Catalyst synthesis

Hexaaluminates. Hexaaluminates were prepared by using both NH_4OH and $(NH_4)_2CO_3$ coprecipitation.

NH_4OH coprecipitation. Two series of catalysts were prepared using a NH_4OH coprecipitation method. The first series was based on Ba–Mn hexaaluminates and the second series was synthesized based on La–Sr–Mn hexaaluminates. Briefly, the metal nitrates in the correct stoichiometric proportion were dissolved in distilled water. The precipitations were then performed by adding the metal solution and the ammonium hydroxide solution simultaneously at room temperature, while maintaining pH=9, into a well-stirred container of distilled water. The solution mixtures were washed with distilled water and filtered. The precipitates were dried at 120°C for 15 h followed by calcination at 1200°C for 2 h.

$(NH_4)_2CO_3$ coprecipitation. In the $(NH_4)_2CO_3$ coprecipitation method for hexaaluminate synthesis, nitrate salts of the metals were dissolved and coprecipitated with ammonium carbonate. Metal nitrates (from Johnson Matthey) were dissolved individually in ~60°C deionized water. Clear solutions of metal nitrates (except aluminium nitrate) were then mixed together, followed by adjusting the pH value to ~1 with nitric acid before adding the aluminium nitrate solution into the metal nitrate mixture. The resulting solution was then poured with vigorous stirring into the H_2O solution with a large excess of $(NH_4)_2CO_3$ at 60°C to form the hexaaluminate precursor precipitate. During the precipitation, a large amount of CO_2 was released while the pH value of the solution was maintained between 7.5 and 8.0. The resulting gel solution was aged with continuous stirring at 60°C for 3 h followed by filtration and washing with deionized water. The filtration cake obtained was then dried at 110°C in air overnight. The powders obtained were calcined at 500°C for 2 h followed by calcination at 1200°C, 1300°C or 1400°C for 2–5 h.

Pd-supported catalysts. 2 wt% Pd was supported on $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ (x=0.0, 0.4, 1.0) and γ-Al_2O_3 using the impregnation method with palladium nitrate (from Johnson Matthey), $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ hexaaluminates were calcined at 1400°C for 5 h before the impregnation.

2.2. Characterization

A combination of bulk and surface-sensitive techniques was used to characterize the catalysts synthesized. The purpose of this characterization was to relate the catalytic activity of the material to its physical and chemical properties. The analytical techniques used include BET and X-ray diffraction (XRD). BET surface areas were measured by nitrogen physisorption at −196°C using Quanta Chrome-NOVA 1000. Powder XRD patterns of the catalysts were measured by using a Philips X'pert System X-ray

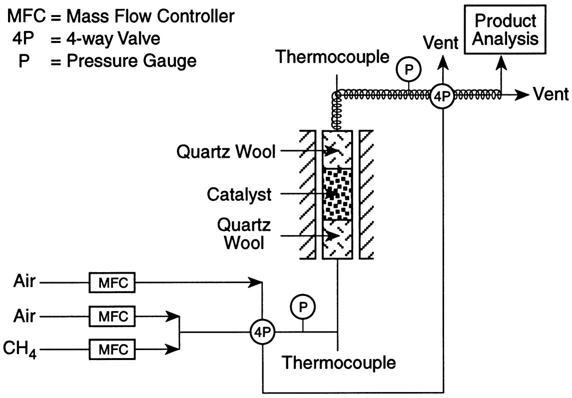

Fig. 1. Schematic of the reactor system.

diffractometer with monochromatized radiation. The XRD instrument was operated at 40 kV and 30 mA. The spectra were scanned between 10°C and 80°C (2Θ) at the rate of 2.4°C/min.

2.3. Reactor system

A fixed-bed laboratory-scale reactor system was designed and constructed for this study. Fig. 1 shows the schematic of this reactor system. The reactor consists of a 3/8 in. ID and 18 in. long alumina tube. The reactor is heated in a single zone tube furnace and the temperature is controlled to $\pm1^\circ$C by a temperature controller. The catalyst bed, supported on quartz wool, is in the middle of the heated zone of the furnace.

The gas flow rates are controlled by electronic mass flow controllers (MFCs). Two four-port valves before and after the reactor were used to flow the reactant mixture through the bypass or through the reactor. The tests for CH_4 oxidation activity were carried out by loading 0.47 g of the catalysts with 1 g of quartz beads in the center of an alumina tube reactor. To study the CH_4 conversion versus temperature, 550 cm^3/min of 1% CH_4 in air was used unless otherwise specified.

Effluent gases are analyzed on-line using an HP 5890 II GC equipped with a thermal conductivity detector (TCD). An 80486 personal computer with HP Chemstation software is used to control the gas chromatography's injection, separation, and detection. The effluent gases are analyzed for CH_4, O_2, CO, and CO_2 using a $9' \times 18''$ 60/80 mesh Hayesep R column and a $6' \times 18''$ 45/60 mesh molecular sieve 5A column.

3. Results and discussion

3.1. X-ray diffraction

Although the characteristic hexaaluminate phases were found in the samples prepared with the NH_4OH coprecipitation method, α- and γ-alumina phases were identified as the major phases for some of this series of catalysts. In the samples prepared with the $(NH_4)_2CO_3$ coprecipitation method, the characteristic hexaaluminate phase was the only phase. The XRD spectra of $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ synthesized by $(NH_4)_2CO_3$ coprecipitation method show hexaaluminate characteristic peaks as shown in Fig. 2.

3.2. BET surface area

The catalysts synthesized by NH_4OH and $(NH_4)_2CO_3$ coprecipitation include Ba–Mn and Sr–La–Mn hexaaluminates. The surface area of these catalysts calcined at 1200°C/2 h ranges from 8.8 to 50.8 m^2/g (Table 1). The surface area of hexaaluminates synthesized by the $(NH_4)_2CO_3$ coprecipitation method, in general, is much higher than the hexaaluminates synthesized by the NH_4OH coprecipitation method. For example, the surface area of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ synthesized by $(NH_4)_2CO_3$

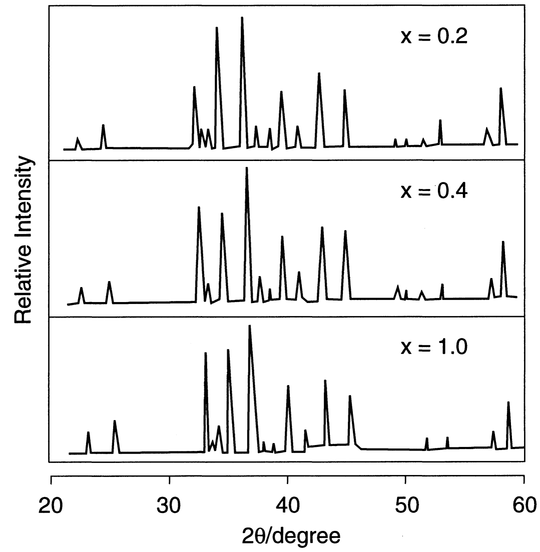

Fig. 2. X-ray diffraction patterns of $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$.

Table 1
Surface area of hexaaluminates prepared by NH_4OH and $(NH_4)_2CO_3$ coprecipitation methods and calcined at 1200°C for 2 h

	NH_4OH	$(NH_4)_2CO_3$
$BaAl_{12}O_{19-\alpha}$	38.1	24.2
$BaMn_{0.5}Al_{11.5}O_{19-\alpha}$	22.5	24.4
$BaMnAl_{11}O_{19-\alpha}$	4.5	27.2
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$	8.8	50.8

coprecipitation is 50.8 m^2/g versus 8.8 m^2/g when synthesized by NH_4OH coprecipitation as shown in Table 1. The surface area difference between catalysts prepared by these two methods is not caused by the differences in crystalline structure of catalysts, because the XRD scans for $Sr_{1-x}La_xMnA_{11}O_{19-\alpha}$ catalysts prepared by these two methods are nearly identical. It was reported by Arai et al. [10] that the surface area of hexaaluminate depends on its crystal morphology. As shown in Fig. 3, hexaaluminate consists of close-parked spinel blocks containing oxygen which are separated by mirror planes containing large cations. The crystal growth of hexaaluminate is suppressed along [0 0 1] direction as compared to [1 0 0] direction resulting in high surface area at elevated temperatures. The surface area of hexaaluminates, therefore, depends on the thickness of the hexagonal facet of hexaaluminate crystals as reported by Arai et al. [10].

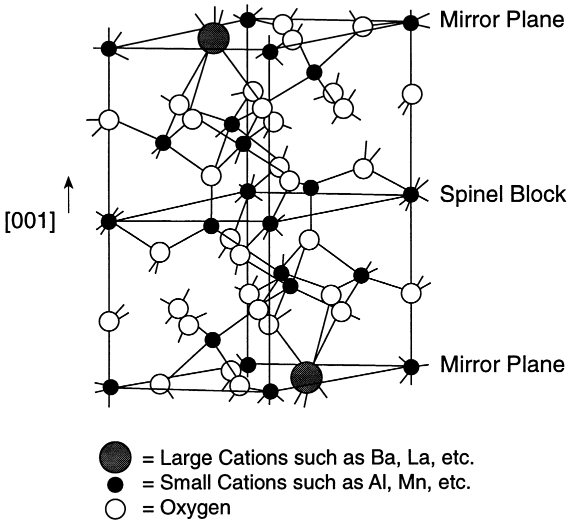

Fig. 3. Hexaaluminate resists sintering along the [0 0 1] direction.

Table 2
BET surface areas and methane oxidation activity of the catalysts synthesized by NH_4OH coprecipitation and calcined at 1200°C

Catalysts	BET surface area (m^2/g)	$T_{10\%}$ (°C)[a]
$BaAl_{12}O_{19-\alpha}$	38.1	~650
$LaAl_{11}O_{18}$	17.4	~650
$Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$	8.8	~550

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/g h space velocity.
[a] Temperature required for 10% CH_4 conversion.

3.3. CH_4 oxidation

The CH_4 oxidation activity, measured as the temperature required for 10% CH_4 conversion ($T_{10\%}$) at 70 000 cm^3/h g space velocity, is shown in Table 2 along with the surface areas for catalysts synthesized by NH_4OH coprecipitation method. All catalysts except $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ show low activity for CH_4 oxidation, with $T_{10\%}$ at about 650°C or higher. Although $BaAl_{12}O_{19-\alpha}$ has the highest surface area among the catalysts synthesized, its CH_4 oxidation activity is low. On the other hand, the surface area of $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ is relatively low (8.8 m^2/g); its CH_4 oxidation activity, however, is the highest with $T_{10\%}$ at about 550°C. This demonstrates that surface area is not the only factor affecting the CH_4 oxidation activity of catalysts. In fact, the rate of the oxidation/reduction cycle and the oxygen desorption capacity of catalysts are also important for low-temperature oxidation of CH_4, as demonstrated by Machida et al. [13].

However, for the same nominal catalytic composition synthesized by the carbonate and hydroxide methods, it would be expected that the oxidation activity of the catalyst with the higher surface area would be higher than the catalyst with lower surface area. Fig. 4 shows the results of CH_4 oxidation activity over $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ synthesized by two different coprecipitation methods. The catalyst synthesized by the hydroxide method has a surface area of 8.8 m^2/g, while the catalyst prepared by carbonate method has a surface area of 50.8 m^2/g (Table 1). The advantage of the $(NH_4)_2CO_3$ coprecipitation method is apparent. $T_{10\%}$ was lowered to <500°C from ~550°C by using the $(NH_4)_2CO_3$ coprecipitation method instead of the NH_4OH coprecipitation method, presumably due to the higher surface area of the catalysts prepared by carbonate coprecipitation.

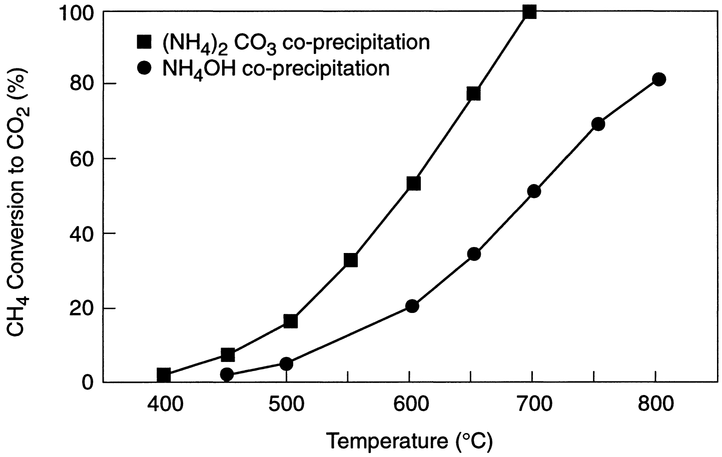

Fig. 4. CH_4 oxidation over $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ hexaaluminate catalysts synthesized by $(NH_4)CO_3$ coprecipitation and NH_4OH coprecipitation.

Ba–Mn series hexaaluminates. A series of Ba–Mn hexaaluminates was prepared for comparison to the results of Groppi et al. [1]. Ba–Mn hexaaluminates were reported to have high surface area and high activity for CH_4 oxidation [1]. The CH_4 oxidation activity of the $BaMn_xAl_{12-x}O_{19-\alpha}$ series synthesized by the $(NH_4)_2CO_3$ coprecipitation method are shown in Fig. 5. The CH_4 oxidation activity decreases in order x=1.0>x=0.5>x=0.0 for $BaMn_xAl_{12-x}O_{19-\alpha}$, as reported by Groppi et al. [1] and Arai et al. [15]. The rate of the surface oxidation/reduction cycle of Mn in $BaMn_xAl_{12-x}O_{19-\alpha}$ was reported to be the key to the high oxidation activity for this series of hexaaluminates [15]. The results here demonstrate the reproducibility of the $(NH_4)_2CO_3$ coprecipitation method for the preparation of high activity hexaaluminates.

Sr–La–Mn series of hexaaluminates. A series of Sr–La–Mn hexaaluminates was also prepared using the $(NH_4)_2CO_3$ coprecipitation method to study the CH_4 oxidation activity. The surface area and CH_4 oxidation activity of this series are summarized in Tables 3 and 4, respectively. We know of no previous report of the synthesis of Sr–La–Mn hexaaluminate series using the

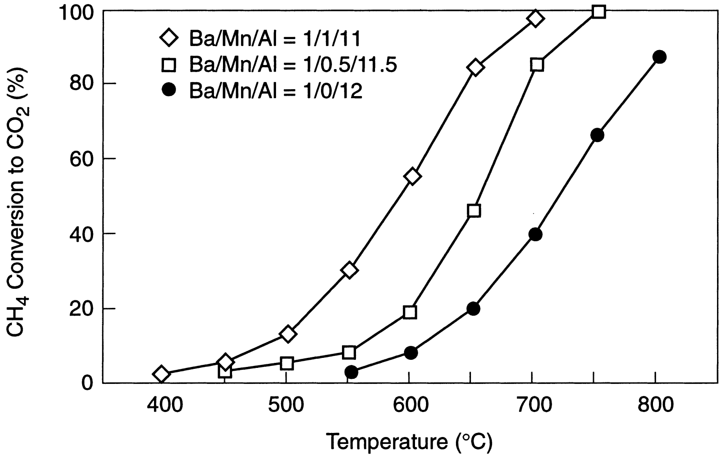

Fig. 5. CH_4 oxidation over $BaMn_xAl_{12-x}O_{19-\alpha}$ hexaaluminate catalysts.

Table 3
BET surface areas of $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ after high-temperature calcination for 2 h

$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$	1200°C	1300°C	1400°C
x=0.0	43.2	23.2	15.8
x=0.2	50.8	23.6	12.9
x=0.4	40.2	18.2	14.3
x=0.6	31.0	17.0	12.4
x=0.8	30.8	23.2	18.1
x=1.0	34.3	23.1	19.3

Table 4
CH_4 oxidation activity of $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ calcined at 1400°C

$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$	x=0.0	x=0.2	x=0.4	x=1.0
$T_{10\%}$ (°C)[a]	480	480	500	450

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/h g space velocity.
[a] Temperature required for 10% CH_4 conversion.

$(NH_4)_2CO_3$ coprecipitation method in the literature, although this series of materials was studied by Arai and his coworkers [13,20] using the alkoxide hydrolysis method. They first reported that an Sr fraction of 0.8 (x=0.2, $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$) had the highest surface area and highest CH_4 oxidation activity in the series [13]. But, recently, they reported that $LaMnAl_{11}O_{19-\alpha}$ (x=1.0) is more active than $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ (x=0.2) for CH_4 oxidation [20]. Our results are similar to those published recently by Eguchi et al. [20]. Table 3 shows the surface areas of $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ ranging from 13 to 50 m^2/g with a Sr fraction from 0.0 to 1.0, which is similar to those obtained using the alkoxide hydrolysis method [13]. $Sr_{0.8}La_{0.2}MnAl_{11}O_{19-\alpha}$ did not show the highest surface area among the $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ series prepared by $(NH_4)CO_3$ coprecipitation (Table 3), as reported by Machida et al. [13] for the alkoxide hydrolysis, nor does the CH_4 oxidation activity increase with surface area (Table 4). $LaMnAl_{11}O_{19-\alpha}$ showed the highest activity for CH_4 oxidation in our study similar to the results reported by Eguchi et al. [20] with $T_{10\%}$=450°C after calcination at 1400°C/2 h (Table 4). This is the highest activity for CH_4 oxidation reported so far in the literature after calcination at 1400°C. Again, the results demonstrate that the hexaaluminates prepared by $(NH_4)_2CO_3$ coprecipitation method are as active and stable as those prepared by the alkoxide hydrolysis method. The relatively simple preparation procedure of the $(NH_4)_2CO_3$ coprecipitation method suggests that it has economic advantages over the alkoxide hydrolysis method.

Usually, the higher the calcination temperature the lower the surface area and CH_4 oxidation activity of catalysts is expected. $LaMnAl_{11}O_{19-\alpha}$ calcined at 1400°C/2 h had higher CH_4 oxidation activity than $BaMnAl_{11}O_{19-\alpha}$ calcined at 1200°C/2 h, as shown in Fig. 6. The results suggest that $LaMnAl_{11}O_{19-\alpha}$ will be much more active for CH_4 oxidation than $BaMnAl_{11}O_{19-\alpha}$ if both catalysts were calcined at

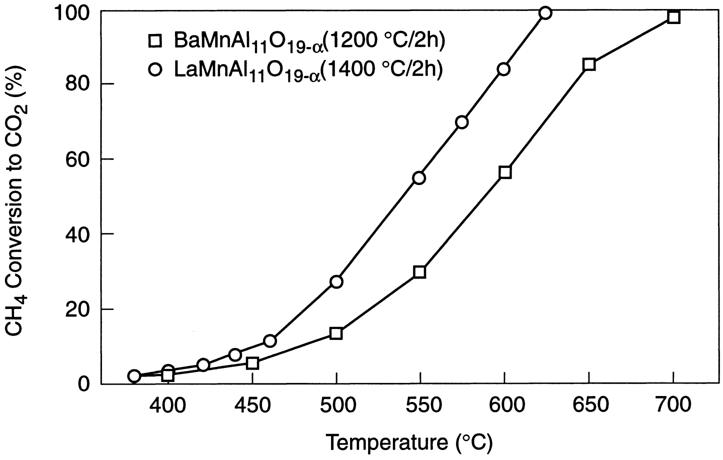

Fig. 6. CH_4 oxidation over $BaMnAl_{12-x}O_{19-\alpha}$ calcined at 1200°C/2 h and $LaMnAl_{11}O_{19-\alpha}$ calcined at 1400°C/2 h.

Table 5
Activation energy for CH_4 oxidation over $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ catalysts

$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$	x=0.0	x=0.4	x=1.0
Activation energy (kcal/mol)	20.2	20.7	19.6

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/h g space velocity.

the same conditions. As pointed out earlier, the ease of the oxidation/reduction cycle of $Mn^{+2}\leftrightarrow Mn^{+3}$ is important for high oxidation activity [13]. Replacing Ba by La increases the CH_4 oxidation activity, as shown in Fig. 6, suggesting the importance of the co-cations in the oxidation/reduction cycle of Mn.

The activation energies of CH_4 oxidation over various $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ hexaaluminate catalysts are shown in Table 5. For all cases, the apparent activation energy is around 20 kcal/mol in the 350–450°C temperature range, suggesting a similar catalytic reaction mechanism regardless of La substitution, at least at these lower temperatures. The activation energy was not affected by the amount of Sr in the hexaaluminate catalysts as it is in a comparable series of perovskite catalysts [17]. However, the similar activation energies determined over both hexaaluminates and perovskites (20.1–26.0 kcal/mol [17]) suggests a similar mechanism for CH_4 oxidation over these two classes of catalyst.

A 100 h run to test the ability of $LaMnAl_{11}O_{19-\alpha}$ was carried out at a 600°C inlet temperature with 1% CH_4 in air and 70 000 cm^3/h g space velocity. The activities at 380–560°C inlet temperatures were also obtained before and after the 100 h run to examine the effect on low-temperature activity. The results are summarized in Table 6 and Fig. 7. Table 6 shows that the initial CH_4 conversion at 600°C of 80.9% decreased only to 79.3% conversion after 100 h. It suggests that the $LaMnAl_{11}O_{19-\alpha}$ is stable under catalytic combustion conditions at 600°C. The low-temperature activity also changed slightly, decreasing from 3.6% to 2.3% at 400°C after the 100 h run, corresponding to an increase in $T_{10\%}$ from 450°C to 460°C after 100 h (Fig. 7).

Table 6
Stability test of $La_xMnAl_{11}O_{19-\alpha}$ for CH_4 oxidation

	CH_4 conversion at	
	600°C	400°C
Fresh (%)	80.9	3.6
100 h on stream (%)	79.3	2.3

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/h g space velocity; catalyst calcined at 1400°C/2 h.

Comparison between hexaaluminates and perovskites. Perovskites are reported to have high activity for CH_4 oxidation [8,11]. Their surface areas are somewhat lower than those of the hexaaluminates. $Sr_{0.25}La_{0.75}CoO_3$ (designated as Sr-0.25) perovskite which calcined at 900°C for 10 h has a surface area of 3.5 m^2/g. Subsequent calcination of the same sample at 1200°C for 2 h resulted in 1.1 m^2/g of surface area [8]. The CH_4 oxidation activities of perovskites and hexaaluminates prepared by $(NH_4)_2CO_3$ coprecipitation were compared. The CH_4 oxidation activity of Sr-0.25 calcined at 900°C/10 h and 1200°C/2 h were both tested. The results are summarized in Fig. 8 and compared to similar results obtained with $LaMnAl_{11}O_{19-\alpha}$ hexaaluminate calcined at 1400°C/2 h. Although the activity of Sr-0.25 calcined at 900°C was somewhat higher than $LaMnAl_{11}O_{19-\alpha}$, the activity of the hexaaluminate is much higher than that of the Sr-0.25 perovskite calcined at 1200°C/2 h. This shows that these high surface area hexaaluminates, synthesized by $(NH_4)_2CO_3$ coprecipitation, are more active combustion catalysts than perovskites at conditions expected in turbines.

Pd supported on $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ hexaaluminates. As shown in the previous section, the activity of the $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ series of catalysts was high for CH_4 oxidation after calcination at temperatures from 1200°C/2 h to 1400°C/2 h. $T_{10\%}$ of 450°C for $LaMnAl_{11}O_{19-\alpha}$ calcined at 1400°C/2 h with 70 000 cm^3/h g space velocity. However, further increase of the low-temperature activity is necessary for turbine applications. Thus, 2% Pd on various $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ catalysts were prepared and tested for CH_4 oxidation. To compare the effect of the hexaaluminate support with γ-Al_2O_3, a 2% Pd/γ-Al_2O_3 was also prepared. Before loading the Pd, all supports except γ-Al_2O_3 were calcined at 1400°C. The activity ($T_{10\%}$), surface areas (after calcination of all catalysts, including Pd/γ-Al_2O_3 at 1200°C/2 h), and activation energy of these Pd-supported catalysts are summarized in Table 7. $T_{10\%}$ varies from 360°C to 450°C for all these catalysts. The activity order is $LaMnAl_{11}O_{19-\alpha}>\gamma\text{-}Al_2O_3>SrMnAl_{11}O_{19-\alpha}>Sr_{0.4}La_{0.6}MnAl_{11}O_{19-\alpha}$ for Pd-supported catalysts.

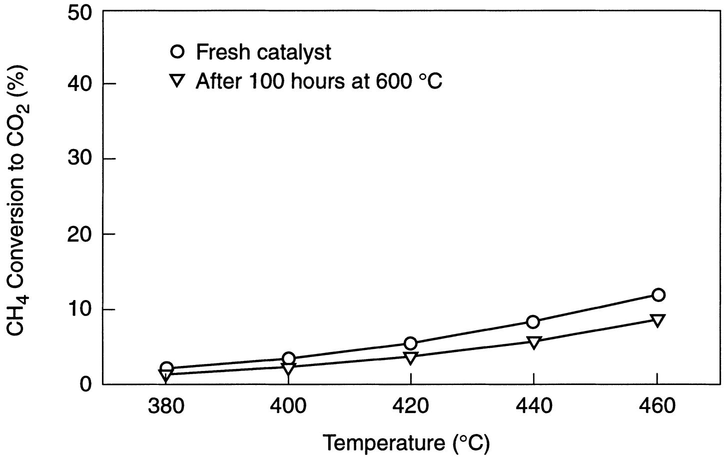

Fig. 7. Low-temperature CH_4 oxidation activities of $LaMnAl_{11}O_{19-\alpha}$ (1400°C) before and after 100 h run at 600°C.

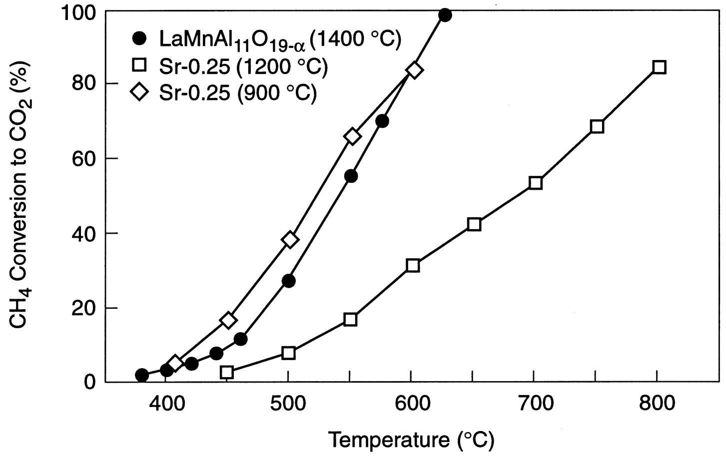

Fig. 8. CH_4 oxidation over $LaMnAl_{11}O_{19-\alpha}$ calcined at 1400°C and Sr-0.25 perovskites calcined at both 900°C and 1200°C.

Table 7
Properties of 2% Pd supported on $Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ hexaaluminates

2% Pd/$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$	x=0.0	x=0.4	x=1.0	2% Pd/γ-Al_2O_3
Surface area at 1200°C (m^2/g)	14.4	13.8	13.7	10.9
$T_{10\%}$ (°C)[a]	420	450	360	410
Activation energy (kcal/mol)	15.5	14.9	15.2	25.3

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/h g space velocity.
[a] Temperature required for 10% CH_4 conversion.

The most active catalyst for CH_4 oxidation with $T_{10\%}$ of 360°C is 2% Pd/$LaMnAl_{11}O_{19-\alpha}$. γ-Al_2O_3 is likely to be transformed to α-Al_2O_3 at temperatures above 1100°C. It results in a lower surface area and, therefore, lower activity for CH_4 oxidation. The results indicate that $LaMnAl_{11}O_{19-\alpha}$ is a better support

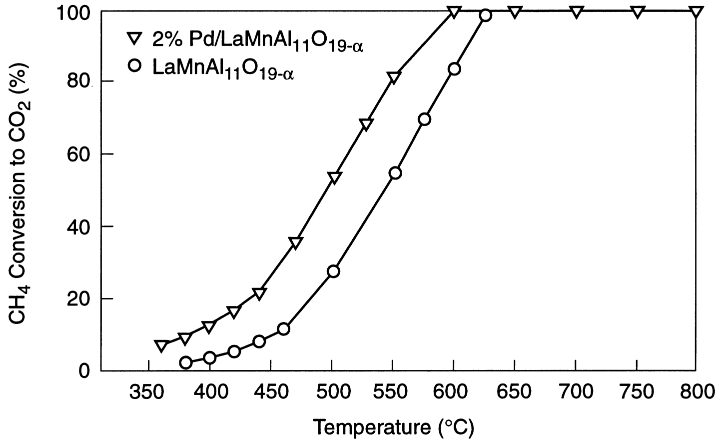

Fig. 9. CH_4 oxidation activities over 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ and $LaMnAl_{11}O_{19-\alpha}$ catalysts calcined at 1400°C.

material than γ-Al_2O_3 for Pd-supported catalysts in the application of catalytic combustion, as expected.

The surface areas of 2% Pd/$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ catalysts were about the same, ~14 m^2/g. A relatively low surface area of 10.9 m^2/g was shown by 2% Pd/γ-Al_2O_3, suggesting significant sintering of the γ-Al_2O_3 support, as expected, due to transformation of γ-Al_2O_3 to α-Al_2O_3. The surface area difference between 2% Pd/γ-Al_2O_3 and 2% Pd/$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ was marginal. On the other hand, the activation energy was significantly different. The activation energy of 2% Pd/$Sr_{1-x}La_xMnAl_{11}O_{19-\alpha}$ was ~15 kcal/mol compared with 25.3 kcal/mol of 2% Pd/γ-Al_2O_3, suggesting that the oxidation mechanism is quite different on the hexaaluminates. A similar wide range of activation energies for Pd supported on various alumina catalysts was reported by Baldwin and Burch [17].

The activities of 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ and $LaMnAl_{11}O_{19-\alpha}$ (with no Pd) are compared side by side in Fig. 9. The 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ has a higher CH_4 oxidation activity than $LaMnAl_{11}O_{19-\alpha}$. It was reported by Farrauto et al. [18] that PdO decomposes to $Pd+\frac{1}{2}O_2$ above 700–800°C, resulting in lower oxidation activity. The reaction inlet temperature of the 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ was intentionally increased to 800°C (as shown in Fig. 9) to

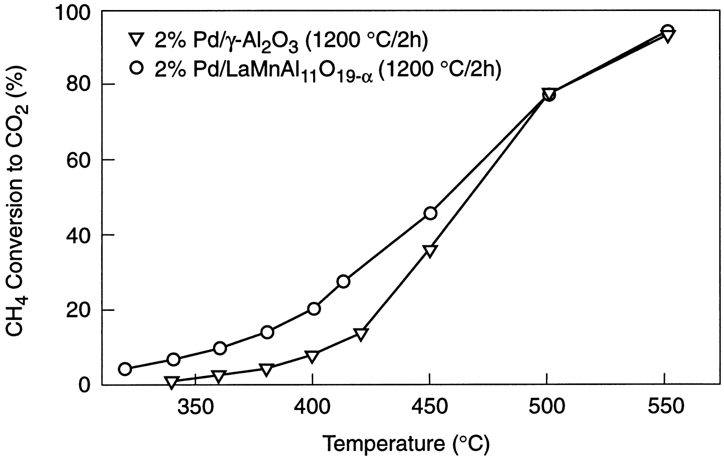

Fig. 10. CH_4 oxidation activities over 2% Pd/Al_2O_3 and 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ catalysts calcined at 1200°C.

Table 8
Stability test of 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ for CH_4 oxidation

	Conversion at indicated inlet temperature	
	525°C	320°C
Fresh (%)	93.0	4.0
100 h on stream (%)	58.9	1.2

Reaction conditions: 1% CH_4 in air, 70 000 cm^3/h g space velocity; catalyst calcined at 1200°C.

determine whether the decomposition of PdO would affect the activity of the catalyst. However, the activity loss resulting from PdO decomposition to Pd did not occur. Apparently the high oxidation activity of $LaMnAl_{11}O_{19-\alpha}$ compensated for the activity loss and complete conversion was observed between 700°C and 800°C.

Fig. 10 shows the activities versus temperature over 2% Pd/Al_2O_3 and 2% Pd/$LaMnAl_{11}O_{19-\alpha}$. The 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ is more active than 2% Pd/γ-Al_2O_3 for oxidation at low temperatures. However, as the temperature increases, the difference between the two catalysts decreases. At 500°C and above, the activity of 2% Pd/γ-Al_2O_3 is the same as 2% Pd/$LaMnAl_{11}O_{19-\alpha}$, i.e., the effect of support on CH_4 oxidation is prominent at low temperatures but not at higher temperatures.

A 100 h run over the most active catalyst (2% Pd/$LaMnAl_{11}O_{19-\alpha}$) was also carried out. The results are very different from the results of $LaMnAl_{11}O_{19-\alpha}$. Table 8 shows that the stability of 2% Pd/$LaMnAl_{11}O_{19-\alpha}$ was poor. The activity at 525°C inlet temperature was 93% in the beginning but dropped to 58.9% after 100 h. The deactivation is likely to be caused by sintering of Pd under reaction conditions, but not because of the decomposition of PdO, the active species for CH_4 oxidation, because the decomposition of PdO only proceeds at temperatures above 700°C [19]. The low-temperature activity measured at 320°C also shows a decrease from 4.0% to 1.2% after a 100 h run at 525°C. If the decomposition of PdO is the cause of deactivation during a 100 h run at 525°C inlet temperature (surface temperature could be much higher), the activity at low temperature should not decrease because Pd can be reoxidized at low temperatures. The results suggest that although the activity of Pd-supported hexaaluminates is high at low temperatures, its stability is poor at high temperatures.

4. Conclusions

The surface area of hexaaluminates obtained from $(NH_4)_2CO_3$ coprecipitation method is higher than the surface area obtained from NH_4OH coprecipitation method and is comparable with the alkoxide preparation method. $LaMnAl_{11}O_{19-\alpha}$ prepared by $(NH_4)_2CO_3$ coprecipitation method showed higher stability and activity than perovskites and $BaMn_xAl_{12-x}O_{19-\alpha}$ after high-temperature calcination. The light-off temperature ($T_{10\%}$) for $LaMnAl_{11}O_{19-\alpha}$ (calcined at 1400°C) is 450°C with 70 000 cm^3/g h space velocity and 1% CH_4 in air. No obvious loss of CH_4 oxidation activity was observed during the 100 h run at 600°C. Pd supported on $LaMnAl_{11}O_{19-\alpha}$ showed even higher activity. $T_{10\%}$ can be lowered to 360°C. However, the stability of Pd/$LaMnAl_{11}O_{19-\alpha}$ was poor. The CH_4 oxidation activity dropped from 93% to 58.9% during the 100 h run at 525°C. With an aqueous method providing another route to prepare the catalysts more efficiently and more cost effectively, $LaMnAl_{11}O_{19-\alpha}$ may be a candidate for catalytic gas turbine combustors.

Acknowledgements

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