Available online at www.sciencedirect.com

Catalysis Today 112 (2006) 157–160

www.elsevier.com/locate/cattod

A comparison between hexaaluminates and perovskites for catalytic combustion applications

Anders Ersson *, Katarina Persson, Isaac Kweku Adu, Sven G. Järås

Kungliga Tekniska Högskolan, Department of Chemical Engineering and Technology, Chemical Technology,
SE-100 44 Stockholm, Sweden

Abstract

Hexaaluminates and perovskites are two promising candidates for use in catalytic combustion applications. In the present study two hexaaluminates, $LaMnAl_{11}O_{19}$ and $LaCoAl_{11}O_{19}$, were compared with two perovskites, $LaMnO_3$ and $LaCoO_3$, with respect to their thermal stability and catalytic activity for combustion of methane and gasified biomass. The results showed that the hexaaluminates retained a much higher surface area even after calcination at 1200 °C compared to the perovskites. $LaMnAl_{11}O_{19}$ showed the highest catalytic activity of all catalysts. $LaCoAl_{11}O_{19}$ generally showed low activity. Of the two perovskites, $LaCoO_3$ was the most active, and the initial test run the activity for biomass combustion were close to that one of $LaMnAl_{11}O_{19}$ even though its surface area was only one tenth of the hexaaluminate's. However, it was severely deactivated in the second test run. Similar deactivation but less severe was also found for the other catalyst.

Keywords: Hexaaluminate; Perovskite; Cobalt; Manganese; Catalytic combustion; Gasified biomass; Methane

1. Introduction

Catalytic combustion is a promising technique for lowering emissions from combustion sources. The catalyst's ability to lower the activation energy of the combustion process makes it possible to decrease the combustion temperature below the threshold temperature for formation of nitrogen oxides, without the stability problems experienced in conventional lean combustion [1]. In order to commercialise catalytic combustion two major problems have to be solved, i.e. finding sufficiently active catalysts and finding materials that can survive prolonged operation at temperatures close to or above 1000 °C [2]. To solve the stability problems several materials have been proposed. Two of the most successful candidates are hexaaluminates, general formula $ABAl_{11}O_{19}$, and perovskites, general formula ABO_3. Even though both of them are promising oxidation catalysts, direct comparison of the activities and thermal stability are scarcely reported in the literature.

The hexaaluminates was first proposed for use as catalytic materials in the late 1980s by Arai and co-workers [3]. The unique layered crystal structure retards the sintering of the material and hence makes them good candidates for use at extreme temperatures [4–6]. The structure also allows for a vide variety of substitutions of metals into the lattice and hence the possibility to tailor the properties of the materials. For combustion catalysts manganese have turned out to be one of the best candidates for B-ion, and many studies have shown manganese substituted hexaaluminates to be the prime choice for methane combustion [7–9].

The perovskites has, like the hexaaluminates, been found to have promising catalytic activity. As for the hexaaluminates their structure allows for a multitude of substitutions in to their crystal structures [10,11]. However, the cubic crystal structure of the perovskite does not hinder the sintering of the materials to the same degree as for the hexaaluminates, and hence may limit their use in high temperature applications [12]. Oxidation reactions over the perovskites have been found to follow two routes either incorporating surface adsorbed oxygen species or incorporating the mobility of lattice oxygen and a redox cycle of the B-ion [13]. As mentioned before only few comparisons have been made between the two materials. Zwinkels et al. did

---

* Corresponding author. Tel.: +46 8 790 66 04; fax: +46 8 10 85 79.
E-mail address: ersson@ket.kth.se (A. Ersson).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.024

compare the surface areas of several different complex metal oxides, including both hexaaluminates and perovskites and concluded that the hexaaluminates retained far larger surface areas at high temperatures than its perovskite counterparts [14].

The objective of this work is to compare the activities for hexaaluminate and perovskite-based catalysts for total oxidation of methane and gasified biomass. Further, the thermal stability, i.e. the surface areas, of the materials are studied and compared.

2. Experimental

2.1. Preparation of the catalysts

The washcoat materials used in this study were all prepared using a co-precipitation technique similar to the one used earlier at our laboratory for preparation of hexaaluminates [15]. Stoichiometric amounts of metal nitrates were dissolved in deionised water. In a second solution ammonium carbonate was dissolved, in large excess in deionised water. The metal nitrate solution was added under vigorous stirring while the pH of the carbonate solution was kept constant at 9 by continuous addition of aqueous ammonia solution. The precipitate formed was centrifuged and washed twice with acetone and dried at 70 °C for 12 h. It was then calcined consecutively to 600, 1000 and 1200 °C for 4 h each and samples were withdrawn for analysis. For the perovskites the main part of the powder was withdrawn at 1000 °C and for the hexaaluminates at 1200 °C the powder was mixed with ethanol and ball-milled for 24 h. Cordierite monoliths (400 cpsi, Corning) were then dip-coated with the slurry yielding monoliths with 17 wt.% washcoat. The catalyst was then calcined at 1000 °C for 1 h.

2.2. Characterisation

The BET surface area and pore size distribution were measured on a Micromeritics ASAP 2000/2010 using N_2 adsorption/desorption at liquid N_2 temperature. The crystal phases were identified by powder X-ray diffraction (XRD) using a Siemens Diffractometer 5000, scanning 2θ from 10° to 90° using monochromatic Cu Kα radiation. The crystal phases were identified using JCPDS files.

Table 1
The composition of the gas used in the gasified biomass tests

Component	Concentration (mol%)
H_2	2.0
CO	2.8
CH_4	0.9
CO_2	2.7
H_2O	1.8
O_2	18.9
N_2	70.9

2.3. Activity tests

The catalytic activities for the different catalyst materials were tested in a conventional flow reactor. For the methane tests the temperature was ramped from 450 to 900 °C and down to 450 °C at a rate of 5 °C/min. The space velocity corresponded to 100 000 h^{-1}, and a methane concentration of 1.5 mol% was used. Two consecutive ramps were performed in order to obtain stable conditions. For the tests using synthetic gas from biomass gasification the temperature was increased by 5 °C/min from 100 to 900 °C; a space velocity of 100 000 h^{-1} and an air to fuel ratio, λ, of 4.5 were used. The compositions of the gas used in the test are found in Table 1.

3. Results and discussion

3.1. Catalyst materials

The BET surface areas as well as the crystal phases of the catalyst materials are found in Table 2. The XRD data show that the perovskites crystallize at a much lower temperature than the hexaaluminates. Already after calcination at 600 °C the perovskites showed some crystallinity. For the LCP the phase found after calcination at 600 °C was the desired $LaCoO_3$ phase, while for the LMP the initial phases formed were La_2O_3 and Mn_2O_3. This may explain the higher surface area found for the LMP compared to the LCP at this temperature. After calcination to 1000 °C the final perovskite phases were achieved for both materials. However, it is interesting to note the fact that the LCP showed traces of La_2O_3 and Co_2O_3 after calcination to 1000 °C but not at the lower temperature. The reflection from Co_2O_3 was almost gone at 1200 °C, while some La_2O_3 remained.

Table 2
The BET surface area and crystal phases of the catalyst materials used in the study

Catalyst name	Calcination temperature					
	4 h at 600 °C		4 h at 1000 °C		4 h at 1200 °C	
	BET surface area (m^2/g)	XRD	BET surface area (m^2/g)	XRD	BET surface area (m^2/g)	XRD
LMH	246	Amorphous	101	Amorphous ($LaMnAl_{11}O_{19}$)	27	$LaMnAl_{11}O_{19}$
LCH	172	Amorphous	62	Amorphous ($LaCoAl_{11}O_{19}$)	24	$LaCoAl_{11}O_{19}$
LMP	50	Mn_2O_3, La_2O_3	3.1	$LaMnO_3$	2.4	$LaMnO_3$
LCP	21	$LaCoO_3$	2.6	$LaCoO_3$	1.8	$LaCoO_3$

For the hexaaluminates the materials remained amorphous after calcination at 600 °C and were only slightly crystalline after 1000 °C. The final crystal phase was not formed until calcination at 1200 °C. This is well in accordance with earlier studies showing that the hexaaluminate phase is formed at temperatures above 1100 °C. The surface areas of the catalysts are also shown in Table 2. As can be seen the surface areas of the hexaaluminates are generally much larger than for the corresponding perovskites, both for the lower as well as the higher temperatures. This is well in accordance with results found by other researchers [15].

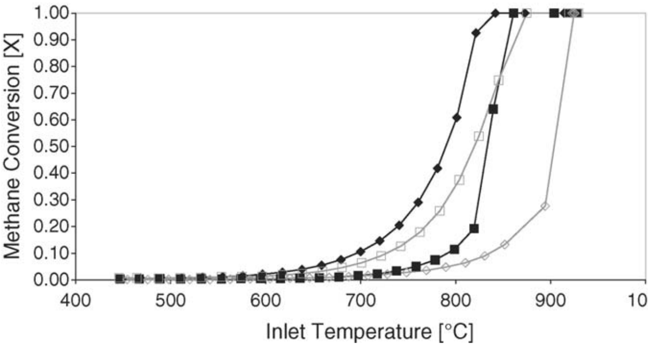

Fig. 1. Conversion of methane over the various catalysts: ◆, LMH ($LaMnAl_{11}O_{19}$); ■, LCH ($LaCoAl_{11}O_{19}$); ◇, LMP ($LaMnO_3$); □, LCP ($LaCoO_3$).

3.2. Activity for catalytic combustion of methane

The activities of the catalysts were tested for total oxidation of methane and synthetic gasified biomass, i.e. a mixture of H_2, CO, CH_4 and CO_2. For both fuels two consecutive ramps were performed in order to assess the deactivation of the catalyst. Earlier experiments at our laboratory have shown that the deactivation after the second ramp is usually low. For the methane tests the differences between the first and the second ramp were very small. Hence, only the conversion of methane for the second ramp is presented in Fig. 1. As can be seen the LMH showed the highest activity for methane combustion, with the temperature 715 °C for 20% conversion. The manganese-substituted catalysts are known for their high activity for methane conversion and many studies have been presented in the literature [4,5,7–9]. The second highest activity was shown by the LCP, with $T_{20\%} = 760$ °C, followed by the LCH with $T_{20\%} = 820$ °C. The manganese perovskite, LMP, showed the lowest activity for methane combustion with $T_{20\%} = 850$ °C; this is very close to the temperature at which homogeneous gas phase reactions become abundant.

3.3. Activity for catalytic combustion of gasified biomass

For the gasified biomass the temperatures for 20% conversion, $T_{20\%}$, and 50% conversion, $T_{50\%}$, of the combustible components of the gasified, i.e. H_2, CO and CH_4, are shown in Table 3. As can be seen, once again the LMH was the most active catalyst in most cases. The only exception was at high conversion of the methane component (>50%) where LCP in the second ramp and LMP in both ramps showed higher activity compared to LMH. Moreover, LCP showed a similar activity as LMH for the oxidation of CO in the fuel during the first ramp. Although the former is likely to be connected with the onset of homogeneous reactions within the catalyst, cf. discussion below. The LCH shows generally poor activity, however the order of ignition of the different components in the biomass was different compared to the other catalysts, i.e. $H_2 < CO < CH_4$ instead of $CO < H_2 < CH_4$ for the LMH, LMP and LCP catalysts. Hence, the LCP was more selective towards H_2 oxidation than the other catalysts. This might prove useful in a catalytic combustor where the heat release has to be carefully controlled.

The high temperatures and reactive fuels involved in catalytic combustion of gasified biomass always imply problems with homogeneous reactions interfering with the heterogeneous reactions. Tests using blank monolith have shown homogeneous reactions to become important at temperatures above 700 °C. However, even if the inlet temperature to the catalyst is lower than 700 °C, the heat release caused by the reaction can cause the onset of homogeneous reactions within the monolith. This was observed for the catalysts with low activity. It is, however, interesting to note that for the more active catalysts, e.g. for LMH and for the first ramp for LCP, the catalytic reactions seemed to suppress the homogenous reactions.

The deactivation between the first and second ramp was much larger for the biomass tests compared than for the methane tests. The most pronounced change was found for the LCP catalyst where the activity for both H_2 and CO decreased

Table 3

The temperatures for 20%, $T_{20\%}$, and 50%, $T_{50\%}$, conversions of the various components of the gasified biomass for the two consecutive ramps

Catalyst	Ramp	$T_{20\%}$ (°C)			$T_{50\%}$ (°C)		
		CO	H_2	CH_4	CO	H_2	CH_4
LMH ($LaMnAl_{11}O_{19}$)	1	385	430	550	440	480	625
LMH ($LaMnAl_{11}O_{19}$)	2	460	520	585	530	565	665
LCH ($LaCoAl_{11}O_{19}$)	1	530	490	695[a]	710[a]	565	720[a]
LCH ($LaCoAl_{11}O_{19}$)	2	685[a]	590	670[a]	740[a]	730[a]	720[a]
LMP ($LaMnO_3$)	1	500	560	600	595	620	625[a]
LMP ($LaMnO_3$)	2	520	600	620	630[a]	630[a]	630[a]
LCP ($LaCoO_3$)	1	385	483	560	430	540	720[a]
LCP ($LaCoO_3$)	2	545	590	595	605[a]	605[a]	605[a]

[a] Indicates likely occurrence of homogeneous reactions inside the monolith.

significantly, while the CH_4 activity increased, the latter most probable due to the onset of homogeneous reactions inside the monolith. For the other catalysts various degrees of deactivation occurred. The increased deactivation compared to the methane test may be connected to the presence of larger amounts of water and carbon dioxide in the gas. Water is well known to increase the sintering rate as well as to form surface hydroxides, while carbon dioxide may form surface carbonates, and thereby poison the active sites. However, more studies are needed to verify the nature of the deactivation process.

4. Conclusions

In this study catalysts based on two hexaaluminates and two perovskites, respectively, were compared as to catalytic combustion of methane and gasified biomass, i.e. a mixture of CO_2, CO, H_2 and CH_4. The following conclusions may be drawn from the study:

- The surface areas of the hexaaluminates were at least one order of magnitude larger than those of the perovskites after calcination at temperatures above 1000 °C.
- The perovskite phase formed at much lower temperature than the hexaaluminate phase.
- For methane the following reaction order was established: LMH > LCP > LCH > LMP.
- For gasified biomass the LMH catalyst was the most active although LCP initially showed a promising activity.
- Contrary to the methane tests significant deactivation occurred between the first and second ramp for the gasified biomass tests. This was especially severe for the LCP catalyst.

The overall conclusion is that for combustion applications $LaMnAl_{11}O_{19}$ seemed to be superior to un-doped perovskites. However, $LaCoO_3$ did show some promising activity especially if its much lower surface area is taken into account.

Acknowledgement

The financial support of Energimyndigheten, the Swedish National Energy Administration, is gratefully acknowledged.

References

[1] E.M. Johansson, D. Papadias, P.O. Thevenin, A.G. Ersson, R. Gabrielsson, P.G. Menon, P.H. Björnbom, S.G. Järås, Catal. Special. Period. Rep., R. Soc. Chem. 14 (1999) 183.
[2] M.F.M. Zwinkels, S.G. Järås, P.G. Menon, T.A. Griffin, Catal. Rev.-Sci. Eng. 35 (1993) 319.
[3] M. Machida, K. Eguchi, H. Arai, J. Catal. 103 (1987) 385.
[4] G. Groppi, C. Cristiani, P. Forzatti, Catal. Special. Period. Rep., R. Soc. Chem. 13 (1997) 85.
[5] K.S. Ramesh, J.J. Kingsley, T.L. Hubler, D.E. McCready, J.L. Cox, in: K.S. Ramesh, et al. (Eds.), Catalyst Materials for High-temperature Processes, The Am. Cer. Soc., Westerville, 1997, pp. 51–69.
[6] H. Arai, K. Eguchi, M. Machida, MRS Int'l. Meeting on Adv. Mat., vol. 2, Materials Research Society, 1989), p. 65.
[7] M. Machida, K. Eguchi, H. Arai, J. Catal. 120 (1989) 377.
[8] G. Groppi, M. Bellotto, C. Cristiani, P. Forzatti, P.C. Villa, Appl. Catal. A: Gen. 104 (1993) 101.
[9] B.W.-L. Jang, R.M. Nelson, J.J. Spivey, M. Ocal, R. Oukaci, G. Marcelin, Catal. Today 47 (1999) 103.
[10] L.G. Tejuca, J. Less-common Met. 146 (1989) 251.
[11] L.G. Tejuca, J. Less-common Met. 146 (1989) 261.
[12] D.M. Lowe, M.I. Gusman, J.G. McCarty, in: G. Poncelet, et al. (Eds.), Preparation of Catalysts VI,, Elsevier, Amsterdam, 1994.
[13] E. Campagnoli, A. Tavares, L. Fabrini, I. Rossetti, Y.A. Dubitsky, A. Zaopo, L. Forni, Appl. Catal. B 55 (2005) 133.
[14] M.F.M. Zwinkels, S. Druesne, G. Menon, E. Björnbom, S.G. Järås, Ind. Eng. Chem. Res. 37 (1989) 391.
[15] A.G. Ersson, E.M. Johansson, S.G. Järås, in: B. Delmon, et al. (Eds.), Studies in Surface Science and Catalysis, vol. 118, Elsevier, Amsterdam, 1998, p. 601.