Catalysis Letters Vol. 79, Nos. 1–4, April 2002 (© 2002)

The effect of chelating agent on the catalytic and structural properties of $Sm_2Zr_2O_7$ as a methane combustion catalyst

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Received 6 September 2001; accepted 27 November 2001

The $Sm_2Zr_2O_7$ of pyrochlore structure was studied as a catalyst for high temperature combustion. It was prepared by the sol-gel method with and without acetylacetone as a chelating agent. The order of crystallinity and the surface area were improved when acetylacetone was used. The catalytic activity of CH_4 combustion was also enhanced and superior to that of Mn-substituted hexaaluminate above 550 °C.

KEY WORDS: $Sm_2Zr_2O_7$; high temperature combustion; sol-gel method; methane combustion.

1. Introduction

It is well known that combustion catalyst can reduce the temperature of operation from 1500 °C to 1300 °C and suppress the NO_x formation [1]. There have been numerous studies on the application of high-temperature oxidation catalysts in gas-turbine power generation [2,3]. Among the most important properties are high combustion activity at typical combustor inlet conditions, thermal stability and high thermal shock resistance [4]. High activity can be obtained with catalysts that have high catalyst surface area. Various promising materials, stable at high temperatures, have been reported in the literature [5]. A series of hexaaluminate was developed by Machida *et al.* [6]. Their sol-gel synthesized hexaaluminate ($BaAl_{12}O_{19}$ and $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$) exhibited a high thermal stability and catalyst activity at high temperature. Groppi *et al.* [7] achieved a similar performance when preparing the Mn-substituted barium hexaaluminate using a coprecipitation method. Pyrochlore ($A_2B_2O_7$) exhibits high chemical stability and catalytic activity at high temperatures in oxidative coupling of methane [8,9]. The application of pyrochlore as a combustion catalyst was recently suggested, as reasonable surface area and catalytic activity were observed in spite of the high temperature treatment for the formation of pyrochlore structure [10]. Also, it is well known that the catalytic performance can be affected by preparation parameters such as chelating ligands, pH, temperature and the mole ration of H_2O to metal alkoxide [11].

In the present study, we investigated the catalytic properties of $Sm_2Zr_2O_7$ pyrochlore material for high temperature combustion. Acetylacetone was used as a chelating agent in the preparation step in order to study the thermal stability and catalytic performance. The catalysts were characterized with XRD, N_2 BET method and SEM.

2. Experimental

2.1. *Catalysty preparation*

2.1.1. *$Sm_2Zr_2O_7$*

$Sm_2Zr_2O_7$ was prepared by hydrolysis method of metal alkoxide. Calculated weight of zirconium isopropoxide (Aldrich, zirconium isopropoxide in isopropanol) was dissolved in 150 ml of isopropanol at 80 °C for 5 h under N_2 atmosphere. The stoichiometric amount of Sm nitrate (Aldrich) and distilled water were dissolved in 50 ml isopropanol. The amount of water was fixed according to the mole ratio of H_2O/M-OR of 2. The latter solution was slowly added to the former solution for about 15 min. This prepared gel was aged 80 °C for 24 h, followed by drying using a rotary evaporator at 80 °C. Dried gel was calcined in the flow of air at the rate of 2 °C/min to 800, 1000 and 1200 °C and further calcined at each temperature for 2 h.

2.1.2. *Modified sol-gel method using acetylacetone as a chelating agent*

The first solution consisted of acetylacetone dissolved in 50 ml isopropanol and the second solution consisted of Zr alkoxide diluted in 50 ml of isopropanol. The ratio of acetylacetone to Zr alkoxide was 2. These two solutions were mixed and refluxed for 1 h at 383 K under vigorous stirring. After cooling the solution at 353 K, the solution

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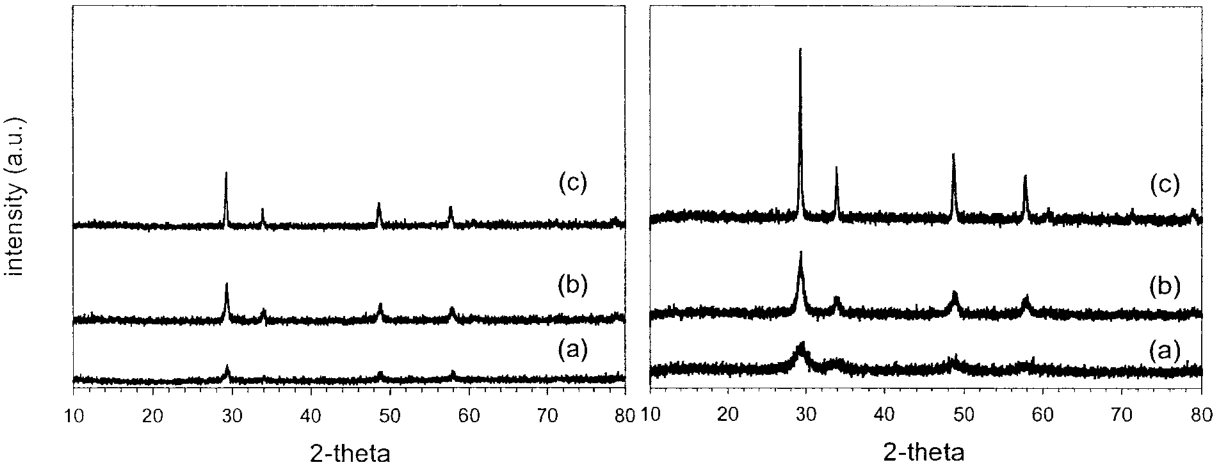

Figure 1. XRD patterns of $Sm_2Zr_2O_7$ calcined at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

containing the $Sm(NO_3)_3$ was added. This prepared gel was aged at 80 °C for 24 h, followed by drying using a rotary evaporator at 80 °C. Dried gel was calcined in the flow of air at the rate of 2 °C/min to 800, 1000 and 1200 °C and further calcined at each temperature for 2 h. The modified $Sm_2Zr_2O_7$ prepared by the sol-gel method in the presence of acetylacetone was denoted as $Sm_2Zr_2O_7$-msg, while $Sm_2Zr_2O_7$ prepared by the sol-gel method without acetylacetone was denoted as $Sm_2Zr_2O_7$-sg.

2.1.3. $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (SLMA)

SLMA was prepared by hydrolysis method in order to compare the catalytic activity and thermal stability with these of prepared pyrochlore catalysts. Detailed procedures are described elsewhere [11].

2.2. Characterization

The surface areas of the samples were measured by the N_2-BET method using a Micromeritics ASAP2010 instrument. X-ray powder diffraction patterns of the calcined sample were recorded in the range of 2θ between 10 and 80° using an X-ray diffractometer (Regaku D/MAX-III). The scan speed was 6°/min. SEM micrographs were taken using Philips 533M with an accelerating voltage of 10 kV.

Catalytic activities were measured in a tubular flow type quartz reactor at atmospheric pressure. Gaseous mixtures of methane (1 vol%) and air (99 vol%) were premixed and fed to the reactor at the space velocity of 20 000 h^{-1}. The methane conversion in the effluent gas was analyzed by on-line gas chromatography (DS6200, porapak Q column, TCD detector).

3. Results and discussion

Figure 1 shows the XRD patterns of $Sm_2Zr_2O_7$-sg and $Sm_2Zr_2O_7$-msg calcined at various temperatures for 2 h. Weak patterns were observed after calcinations at 800 °C for both catalysts. These peaks could be assigned to the characteristic peaks of $Sm_2Zr_2O_7$ structure [12]. The strongest peak observed at 29.2° is assigned to the (222) plane of $Sm_2Zr_2O_7$ of pyrochlores structure. Increasing the calcinations temperature did not change the 2θ angles characteristic of pyrochlore structure but the intensities of each peak increased. This means that during the calcination step, any other impurity oxides such as ZrO_2 and Sm_2O_3 were not formed. The two components (Sm and Zr) in the dried gel existed almost homogeneously. It is well known that sol-gel techniques have an advantage over the conventional solid-state reaction in enhancing the homogeneity in the prepared gel. The $Sm_2Zr_2O_7$-msg showed the peaks more intense than $Sm_2Zr_2O_7$-sg after calcinations at 800, 1000 and 1200 °C indicating that the degree of crystallinity of $Sm_2Zr_2O_7$-msg was much higher than $Sm_2Zr_2O_7$-sg. The surface areas of calcined $Sm_2Zr_2O_7$-sg and $Sm_2Zr_2O_7$-msg are shown in figure 2. Increasing the calcination temperature decreased the surface areas of each $Sm_2Zr_2O_7$ slightly. $Sm_2Zr_2O_7$-msg had a surface

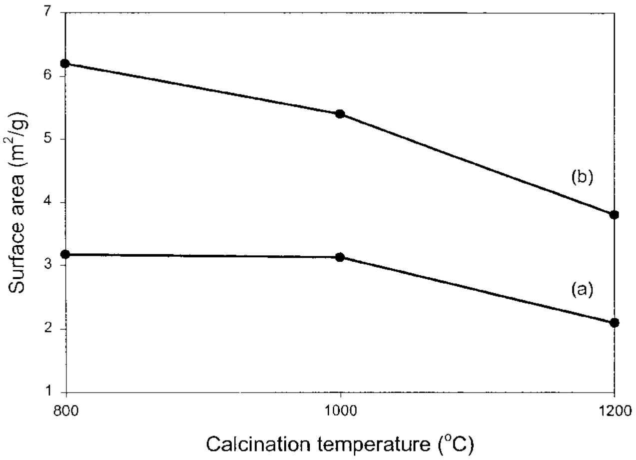

Figure 2. Surface areas of (a) $Sm_2Zr_2O_7$-sg and (b) $Sm_2Zr_2O_7$-msg calcined at various temperatures.

area twice that of the $Sm_2Zr_2O_7$-sg. After calcination at 1200 °C, $Sm_2Zr_2O_7$-msg had a surface area of $4\,m^2/g$. The surface area of pyrochlore structure obtained by solid-state reaction was below $1\,m^2/g$ [13], indicating that the sol-gel method is superior to the solid-state reaction method in the preparation of pyrochlore of high surface area. However, the surface area of calcined $Sm_2Zr_2O_7$ was much smaller than that of SLMA calcined at 1200 °C, which was $15\,m^2/g$.

It is well known that the hydrolysis using the metal alkoxide could be a good method for the preparation of homogeneous metal oxide. If more than two components of metal precursors are involved during the preparation step, the different rate of hydrolysis of each precursor could affect the physical property of the desired product. To achieve the ideal homogeneity of final products, it is important to adjust the rate of each alkoxide in the hydrolysis step [14]. To improve the crystallinity of a desired structure, it should be necessary to control the hydrolysis rate of Zr or Ti alkoxide for high crystallinity of pyrochlore structure. Since these alkoxides are hydrolyzed very rapidly just after adding water, the balanced incorporation of two components into the sol-gel network might be difficult during the aging step. Higher homogeneity was obtained for the SiO_2/TiO_2 mixed oxide system [15] by chemical modification of Ti alkoxide. Also, it is reported that the formation of titanium alkoxide chelates does not significantly influence the hydrolysis rate. However, it lowers the functionality and thus the condensation rate of the hydrolyzed titanium species [16]. It is also well known that chelating agents such as acetylacetone decrease the condensation rate and, to an even greater extent, the hydrolysis rate resulting in bigger voids in the gel with larger pore volume in the final oxide particle [17]. This was confirmed in SEM micrographs as shown in figure 3. $Sm_2Zr_2O_7$-msg consisted of smaller primary particles and had a void volume larger than $Sm_2Zr_2O_7$-sg. The estimated primary particle size for the $Sm_2Zr_2O_7$-msg was about 50 nm. $Sm_2Zr_2O_7$-msg shows a circular void structure formed by the agglomeration of spherical primary particles, while $Sm_2Zr_2O_7$-sg shows the morphology of compact agglomeration of bigger primary particles (300–500 nm).

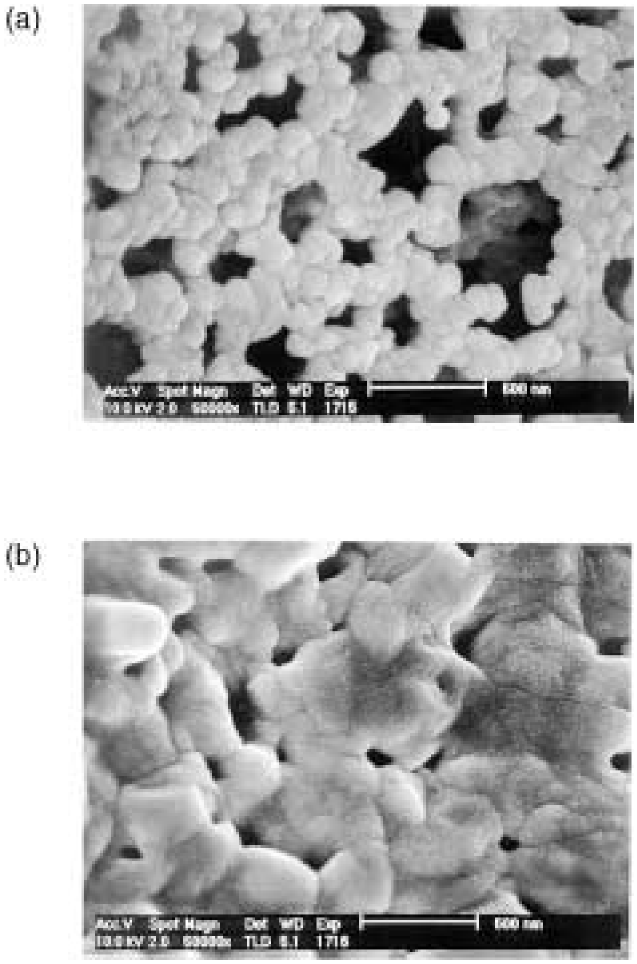

Figure 3. SEM micrographs of $Sm_2Zr_2O_7$ prepared (a) in the presence of and (b) in the absence of acetylacetone, then calcined at 1200 °C.

Figure 4 showed the CH_4 conversion profiles of $Sm_2Zr_2O_7$-sg and $Sm_2Zr_2O_7$-mag. The strong enhancement of catalytic activity was observed for the $Sm_2Zr_2O_7$-msg calcined at 1200 °C. The $T_{10\%}$ and $T_{90\%}$ of $Sm_2Zr_2O_7$-sg calcined at 1200 °C is 530 °C and 730 °C, respectively. The $T_{10\%}$ and $T_{90\%}$ of $Sm_2Zr_2O_7$-msg calcined at 1200 °C is 490 °C and 670 °C, respectively. The catalytic activity of $Sm_2Zr_2O_7$-msg is much higher than that of $Sm_2Zr_2O_7$-sg. As the calcination temperature increased from 1000 °C to 1200 °C, the specific surface area decreased from $6.2\,m^2/g$ to $4.0\,m^2/g$. However, the catalytic activity for CH_4 combustion was not decreased that much. $T_{10\%}$ of SLMA calcined at 1200 °C is 450 °C, which is much lower than that of $Sm_2Zr_2O_7$-msg (490 °C). The catalytic activity of SLMA at lower temperatures contributed largely to the Mn component, which is known to provide a high CH_4 combustion activity at low temperature. However, $T_{90\%}$ of SLMA (720 °C) is much higher than that of $Sm_2Zr_2O_7$-msg (670 °C) indicating that the catalytic activity of $Sm_2Zr_2O_7$-msg is higher than that of SLMA at high temperature. Considering the high surface area of SLMA calcined at 1200 °C ($15\,m^2/g$), the specific catalytic activity of $Sm_2Zr_2O_7$-msg calcined at 1200 °C (surface area = 4.0 m/g) per m^2 is four times as much as that of SLMA.

In summary, $Sm_2Zr_2O_7$ of pyrochlore structure was synthesized by the sol-gel method in the presence of a chelating agent, acetylacetone. The surface area of $Sm_2Zr_2O_7$ prepared by the sol-gel method is much higher than that of $Sm_2Zr_2O_7$ prepared by solid-state reaction. Furthermore, the sol-gel method in the presence of acetylacetone prepared $Sm_2Zr_2O_7$-sg, of which the surface area is twice as much as that of $Sm_2Zr_2O_7$ prepared in the absence of acetylacetone. Acetylacetone reduced the hydrolysis and condensation

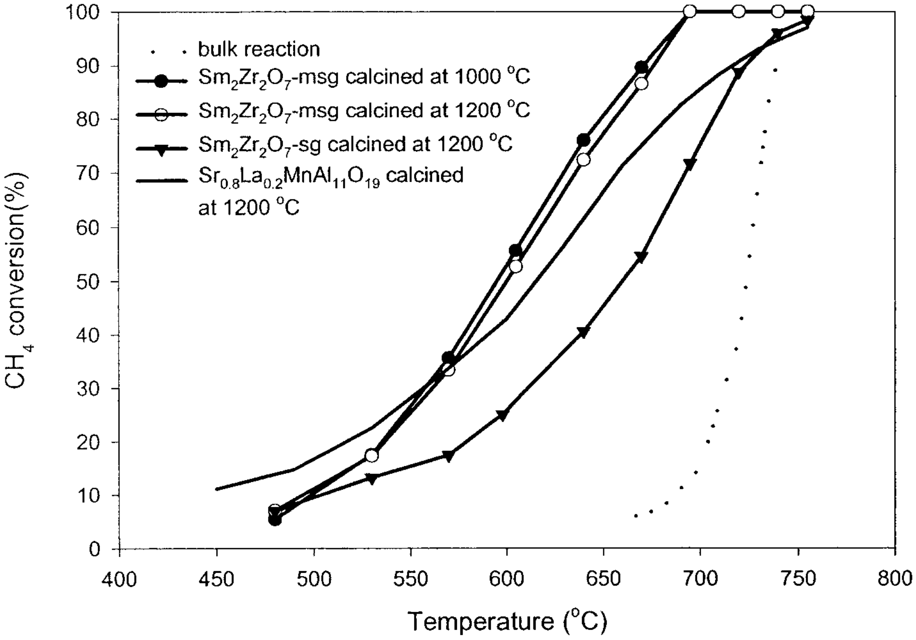

Figure 4. Conversion profiles in the methane combustion catalyzed over $Sm_2Zr_2O_7$ and SLMA.

rate of Zr isopropoxide, resulting in the more open structure and smaller primary particle size. This $Sm_2Zr_2O_7$ is four times more active, based on the activity per m^2, than SLMA which is known to show the highest activity in CH_4 combustion.

Acknowledgment

This study is funded by Center for Ultramicrochemical Process Systems (CUPS) sponsored by KOSEF (2001).

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