EFFECT OF DRYING METHODS ON THE STRUCTURE AND CATALYTIC COMBUSTION ACTIVITY OF Mn-SUBSTITUTED HEXAALUMINATE CATALYSTS


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Abstract

Conventional oven drying (COD) and supercritical drying (SCD) methods were applied to the preparation of Mn-substituted hexaaluminate (BaMnAl\(_{11}\)O\(_{19}\)) catalysts. The effect of drying methods on phase composition, specific surface area, pore structure and combustion activity of the samples was investigated. The samples obtained by SCD have higher surface area, narrower pore size distribution, and higher combustion activity than those obtained by COD.

Keywords: Methane, catalytic combustion, hexaaluminate, supercritical drying

INTRODUCTION

Recently, catalytic combustion has attracted considerable attention due to its potential for burning natural gas and methane in turbines with extremely low levels of NO\(_x\) emissions [1]. The main problem in the development of a catalytic combustion process is in the finding of suitable catalysts with high stability and high activity [2]. Arai and his co-workers reported that manganese-substituted barium hexaaluminate, BaMnAl\(_{11}\)O\(_{19-a}\), showed high activity for methane combustion [3]. Many researchers have made great efforts to...
enhance the catalytic activity of manganese-substituted barium hexaaluminate [4-6], among them, Yan and Thompson synthesized high surface area cation-substituted barium hexaaluminates (BaMnₓCo₁₋ₓAl₁₁O₁₉₋ₓ) by using a supercritical drying procedure [6]. However, few studies have been reported on the effect of drying methods on the preparation and properties of such high-temperature resistant materials. Emphasis of this work has been placed on elucidating the effect of drying methods on the pore structure, surface area, and combustion activity of Mn-substituted hexaaluminate(BaMnAl₁₁O₉₋ₓ).

EXPERIMENTAL

Preparation of catalysts

The sol-gel method used here was similar to the one described by Ersson et al. [7]. The barium and manganese nitrates were dissolved in deionized water. The aluminium isopropoxide powder was dissolved in warm isopropanol. The metal nitrate/water solution was then added to the aluminium isopropoxide solution. The gel/sol so formed was allowed to age for 12 h. The gel obtained was divided into two parts: one part dried in an oven at 110°C for 24 h and the xerogel sample so obtained was designated as Xerogel-110. The other dried by supercritical ethanol (260°C and 8.0 MPa) for 2 h. The aerogel sample so obtained was designated as Aerogel-260. The Xerogel-110 and Aerogel-260 samples were calcined at 500°C for 1 h and followed by calcination at 1200°C for 4 h. The samples after calcination were referred to as Xerogel-1200 and Aerogel-1200, respectively.

Physicochemical characterization

The specific surface area (S_{BET}) and the mean pore diameter (d_{p}) of the samples were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2010 instrument. Pore size distributions were calculated by applying the Barrett-Joyner-Halenda (BJH) method to the desorption branch of the isotherms. Powder XRD characterization was performed with a Rigaku D/MAX-RB X-ray diffractometer using a copper target at 40 kV and 50 mA. TEM images were taken using a JEOL JEM-1200EX microscope.
Catalytic activity tests

The catalytic activity for methane combustion was tested by a fixed-fed quartz reactor system. For each experiment, 1 cm³ of the catalyst (grain size 20 - 40 mesh) was loaded to the reactor (i.d. = 15 mm) by packing quartz beads at both ends of the catalyst bed. 1 % CH₄ in air was used as the feed, and the gas hourly space velocity (GHSV) was monitored to 48,000 h⁻¹. The effluent gases were analyzed for CH₄, air, CO and CO₂ using a carbon molecular sieve column. T₁₀ was used to express the activity for methane combustion, which represents the temperatures required for a 10% conversion of CH₄.

RESULTS AND DISCUSSION

Isotherm, pore structure and specific surface area

The adsorption/desorption isotherms of the Aerogel-260 and Xerogel-110 samples are shown in Fig.1. The Aerogel-260 sample shows a type-IV isotherm with a type-H₃ desorption hysteresis loop according to IUPAC classification [8]. The shapes of the hysteresis loops have often been identified with specific pore structures. The type-IV isotherm is associated with particles giving rise to slit-shaped pores. The Xerogel-110 sample shows a type-IV isotherm with a type-H₂ desorption hysteresis loop. According to the suggestion of IUPAC, this type of hysteresis loop is resulted from crossed pores with narrow necks and wide bodies (often referred to as ‘ink - bottle’ model pores).

As shown in Table 1, the BET surface area of the Xerogel-110 sample was 370.2 m² g⁻¹. After calcination at 1200°C, it decreased to 21.3 m² g⁻¹. Although the BET surface area of the Aerogel-260 sample was 260.5 m² g⁻¹, it reduced to 72.2 m² g⁻¹ after calcination, which is much higher than that (21.3 m² g⁻¹) of the Xerogel-1200 sample.
Table 1
Preparation and morphological properties of BaMnAl$_{11}$O$_{16}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Drying</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerogel-260</td>
<td>SCD$^a$</td>
<td>260.5</td>
<td>1.36</td>
<td>20.9</td>
</tr>
<tr>
<td>Xerogel-110</td>
<td>COD</td>
<td>370.2</td>
<td>0.32</td>
<td>3.5</td>
</tr>
<tr>
<td>Aerogel-1200</td>
<td>SCD</td>
<td>72.2</td>
<td>0.35</td>
<td>19.5</td>
</tr>
<tr>
<td>Xerogel-1200</td>
<td>COD</td>
<td>21.3</td>
<td>0.14</td>
<td>25.5</td>
</tr>
</tbody>
</table>

$^a$SCD-supercritical drying; COD-conventional oven drying.
$^b$VP: pore volume.
$^c$d$_p$: mean pore diameter. $d_p$=4$V_p$/$S_{BET}$

Fig. 2. TEM images of BaMnAl$_{11}$O$_{16}$ catalysts before and after calcination.
(a) Xerogel-110, (b) Aerogel-260, (c) Xerogel-1200, (d) Aerogel-1200

Morphology of the samples before and after calcinations

The morphology of the samples before and after calcination was investigated by transmission electron microscopy (TEM) and the results are
shown in Fig. 2. The particles in the Aerogel-260 sample were fibroid (Fig. 2a), which was obviously different from those in the Xerogel-110 sample (Fig. 2b). After calcination at 1200°C, the Aerogel-1200 powders consist of thin planar crystals, whereas the Xerogel-1200 contained rather thick and large agglomerates [(c) and (d) of Fig. 2]. The larger surface area of Aerogel-1200 sample was maintained due to the thinner hexagonal facet of hexaaluminate crystals.

![XRD patterns of the BaMnAl11O36 catalysts](image)

**Fig. 3.** XRD patterns of the BaMnAl11O36 catalysts
(a) Aerogel-1200 (b) Xerogel-1200
β: β-Al2O3; α: α-Al2O3; S: BaAl2O4

**Effect of drying methods on phase composition**

The XRD spectra of the Aerogel – 1200 and Xerogel – 1200 samples are shown in Fig. 3. The Ba-β-Al2O3 phase was the major phase of the samples. Trace of BaAl2O4 phase existed in both samples. α-Al2O3 could not be found in the Aerogel – 1200 sample (Fig. 3a). However, it existed in the Xerogel – 1200 sample (Fig. 3b). This indicates that the phase composition of the final material could be affected by the drying methods.

It was reported by Machida *et al.* [9] that homogeneous mixing of the components at molecular level could be attained by the sol-gel method via hydrolysis of alkoxides. The formation of the Ba-β-Al2O3 phase is promoted by such homogeneous mixing of the components. For the drying of gel, it is
generally accepted that there are three stages [10], and in stage 2 liquid transport occurs when flowing through the surface film that partially covers the empty pores. The liquid flows to the surface where evaporation takes place. The flowing is driven by the gradient of capillary stress [11]. Migration of the Ba, Mn, and Al species may exist in the conventional oven drying process due to the flowing of the liquid to the surface from the inner pores. Heterogeneous mixing of the components was promoted by the migration of the Ba, Mn, and Al species in water. Such heterogeneous mixing of the components could produce different phases during the preparation of complex oxides. With the supercritical drying, however, the flowing of the liquid to the surface is suppressed, because the capillary stress is eliminated. As a result, migration of the Ba, Mn, and Al species caused by the flowing of the liquid could be avoided, and homogeneous mixing of the components could be maintained.

**Fig. 4.** CH$_4$ combustion over BaMnAl$_{11}$O$_{19}$ catalysts, 1% CH$_4$ in air, GHSV: 48000 h$^{-1}$

**Effect of drying methods on the combustion activity of methane**

The catalytic activity for methane combustion over the BaMnAl$_{11}$O$_{19}$ catalysts obtained by different drying methods was investigated and the results are shown in Fig. 4. The ignition temperature ($T_{10}$) of the Aerogel – 1200 sample was ca. 450°C, which was 20°C lower than that of the Xerogel - 1200 sample. This indicates that the catalytic activity of the Aerogel – 1200 sample was higher than that of the Xerogel - 1200 sample. For the catalysts with the
same composition, surface area is an important parameter of the combustion catalysts. The Aerogel-1200 sample obtained by the supercritical drying has a higher catalytic activity for methane combustion due to its larger surface area.

CONCLUSION

Drying methods have a strong effect on the phase composition, surface area, pore structure and combustion activity of the Mn-substituted hexaaluminate catalysts. With supercritical drying, the homogeneous mixing of the components in the sol-gel process could be maintained. Compared with the samples obtained by COD, those by SCD have higher surface area, narrower distribution of pore sizes and higher combustion activity.

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REFERENCES