PREPARATION, CHARACTERIZATION, AND CATALYTIC DEOXIDATION OF HOLLOW FIBER TYPE $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$CATALYST FOR PRETREATMENT OF LANDFILL GAS

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Abstract - $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$(LSCF-1928)perovskite-type powderwere found to have remarkable catalytic activity and stability for the de-oxidation reaction of landfill gas (LFG) in our previous study.The bead and hollow fiber type catalysts were prepared using theLSCF-1928 powder. In the case of bead type catalyst with methyl cellulose (MC) as organic binder, CO_2 emitted from MC was reacted with strontium, so the $SrCO_3$ was formed. On the other hand, a single phase perovskite structures were formed without impurities when the hollow fiber type catalyst was fabricated without organic binder. Also, pore structure of the hollow fiberwas induced during phase inversion process, so the surface area of catalysts could be increased.Various spinning condition such as air gap and pressure of dope solution were investigated for control the pore size and porosity of the hollow fibers. The SEM images shows the hollow fiber structure which consists of two kinds of morphologies, namely: asymmetric outer skin layer with finger-like macrovoids, and sponge-like structure between the skin layer. All kind of the hollow fiber in this study have above 99.9% O_2 conversion at 475 ^oC. Especially, hollow fiber type catalyst perepared with the condition of dope solution pressure: 7 bar, inner coagulant: 5 ml/min, and air gap: 2 cm has best performance of 70.65, 93.1, and 99.99% O_2 conversion at 425, 450, and 475 ^oC, respectively.

Keywords - Catalyst, Perovskite Oxides, Hollow Fiber, Landfill Gas, Oxygen Removal, Methane Oxidation

I. INTRODUCTION

The atmospheric concentration of greenhouse gas (GHG, Green House Gas) is increasing continuously as a result of the combustion of fossil fuels and industrial development. In response to this trend, many researches have been conducted on the reduction of GHG [1]. Landfill gas (LFG, Landfill Gas) is one of the largest sources of greenhouse gas emissions containing the methane (CH_4) as major constituent and can be considered a renewable resources as well [2,3]. The components of LFG are methane (35-60%), carbon dioxide (30-50%), nitrogen (2-10%), oxygen (0.1-2%) and trace of other gasses (ammonia, hydro sulfide and siloxanes) [4]. Among various contents, oxygen can cause severe corrosion to compressor materials, pipeline and engines [4,5]. In order to avoid these potential problems, the maximum oxygen concentrationswere set between 0.5mol% (Germany) and 0.03 mol% (Korea) in many different countries [6]. Thus, it is necessary to remove oxygen from the LFG to use LFG as renewable fuel.

In our previous work[7], we proposed theperovskite-type oxides with general formula: $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ (Sr = 0.2, 0.4, 0.6, and 0.7) as catalystsfor the deoxygen of LFG at intermediate temperature with the aim to reduce the use of precious and noblemetals. From the results, we found out that LSCF-1928 showed the best catalytic performance for removal of oxygen from LFG. In this work, hollow fiber type catalysts with LSCF-1928 were prepared with various conditions for the deoxidation from LFG. The performance to removal of oxygen from LFG was investigated with different catalyst according to various reaction temperatures

II. DETAILS EXPERIMENTAL

2.1. Preparation of hollow fiber type-perovskite catalysts.

Hollow fiber type perovskite catalysts were prepared by a phase-inversion/sintering technique using commercial $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$powder (Kceracell).The dope solution was prepared form a mixture of 60.52 wt% LSCF-1928 powder, 31.12 wt% 1-methyl-2-2-pyrrolidone (NMP, 99.5%, Samchun Pure Chemical Co., Ltd., Korea), 7.78 wt% polyetherimide (PEI, Sigma-Aldrich, U.S.A), and polyvinylpyrrolidone (PVP, Sigma-Aldrich, U.S.A). NMP, PEI, and PVP acted as solvent, binder, and dispersant, respectively. The spinning pressure of the dope solution was 5-7 bar, inner coagulant flow rate was 5 mL/min, and length of the air gap was 2-10 cm. The spinning process was performed at room temperature. The green body was placed in the water tank for 24 h, and then dried in an oven at 100 ^oC for 24 h. The dried hollow fiber type catalyst were heated in a box furnace at a heating rate of 5 ^oC/min to a temperature of 800 ^oC and were maintained at that temperature for 4h. These fabrication conditions was summarized in Table 1

	Method 1	Method 2	Method 3
Spinning pressure (bar)	5	5	7
Air gap (cm)	2	10	2

Table 1: The summary of fabrication condition

2.2. Characterization of the catalysts.

The X-ray diffraction (XRD) was employed to characterize crystalline phase of catalysts under different fabrication conditions. Samples were scanned over the 2θrange from 20 ^{o} to 80 ^{o} with scan rate 0.02 ^{o} per minute usingRigaku D/Max 2200-Ultimaplus.Observations of morphology of the as-prepared hollow fiber were performed using scanning electron microscopy (SEM, Hitachi S-4800, Japan).

2.3. Catalytic activity measurements

The composition of simulated LFG gas with 50 mol% CH_4, 40 mol% CO_2, 8 mol% N_2, and 2 mol% O_2 was used for feed gas of deoxygen. The reactor consisted of a quartz tube of 20 mm in diameter and 52 cm in length with LSCF catalyst in between inert quartz wool as shown in Fig. 1. Inert quartz pellets were also placed on both sides of the wool to provide better thermal insulation and mixing of the inlet reactant gases. The reactor assembly was installed in an electric furnace and a sample collection system. The amounts of the reaction products were determined by gas chromatography (GC, Agilent 7820N, ShinCarbon ST Columns) with thermal conductivity detector [7]. After dioxygen test, the O_2 conversion was calculated with equation (1).

$$O_2\text{conversion (\%)} = \frac{C_{O_{2,feed}} - C_{O_{2,reacted}}}{C_{O_{2,feed}}} \times 100 \quad (1)$$

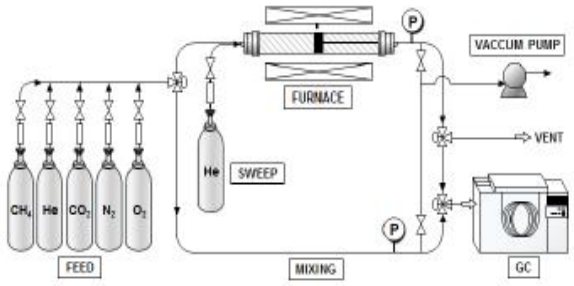


Fig.1. Experimental setup for testing of the deoxygen catalyst

III. RESULTS AND DISCUSSION

3.1. The comparison of bead and hollow fiber type catalyst

Fig. 2 shows the images of bead and hollow fiber type catalyst. The bead type catalyst was prepared with methyl cellulose (MC) as organic binder.

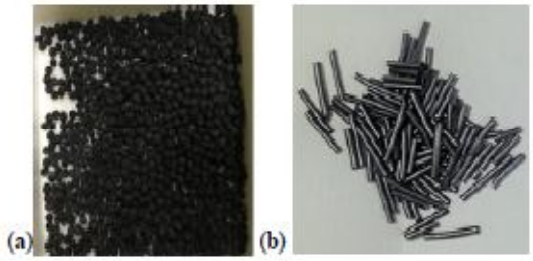


Fig. 2 (a) bead and (b) hollow fiber type LSCF-1928 catalyst

Fig.3 shows that XRD spectra of LSCF powder, bead, and hollow fiber. Hollow fiber type catalyst are indexed with perovskite LSCF structure whilebead type catalyst shows the mixture of strontium carbonate and perovskite LSCF peaks. In the case of bead type catalyst, CO_2 emitted from MC was reacted with strontium, so the $SrCO_3$ was formed as impurity. On the other hand, a single phase perovskite structures were formed without impurities in the hollow fiber type catalyst.

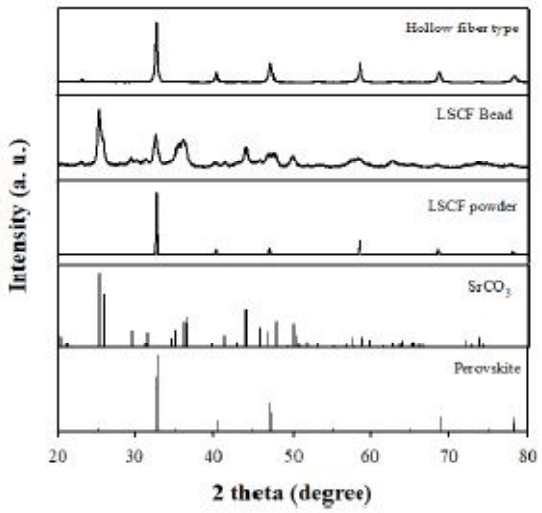


Fig.3. XRD patterns of the prepared LSCF catalyst and standard

Fig. 4 illustrates the morphologies of hollow fiber type catalysts fabricated with different methods.

(a) Method 1(b)Method 2 (c)Method 3

(b)

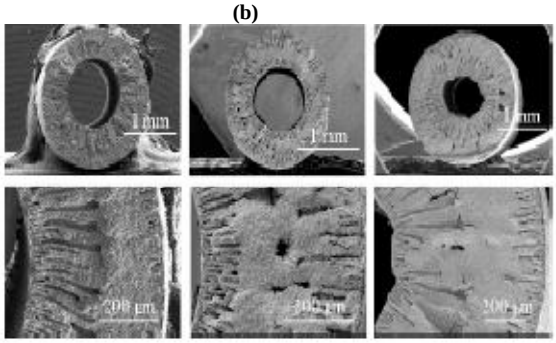


Fig. 4. A scanning electron microscopy (SEM) image of the cross-section of the hollow fiber type catalysts (a) ; (b) ; (c)

As known in Fig. 4, the hollow fiber type catalystsof different methods consist of three kinds of morphologies: asymmetric outer skin layer with finger-like macro pores, and sponge-like structure between the skin layers.

The oxygen conversion was presented in Fig. 5. As the reaction temperature increased, the conversion of hollow fiber type catalysts increased with S shaped curve irrespective of methods. Hollow fiber type catalyst prepared with 7 bar dope solution pressure showed best performance of 70.65, 93.1, and 99.99% oxygen conversion at 425, 450, and 475 ^{o}C, respectively.

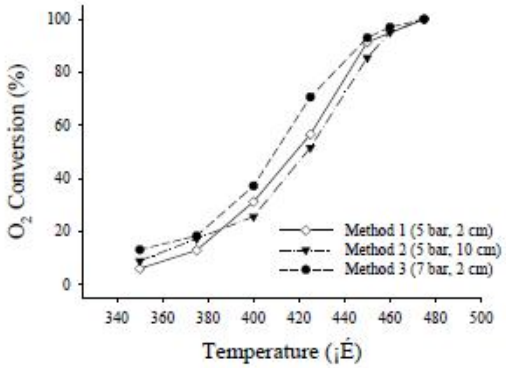


Fig.5. The results of O_2 conversion with LSCF-1928 hollow fiber type catalysts prepared with different method

CONCLUSIONS

Hollow fiber type $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ catalysts were prepared successfully for the de-oxidation reaction of landfill gas (LFG). Hollow fiber type LSCF-1928 catalyst shows single perovskite structure without impurity such as strontium carbonate in comparison with bead type catalyst. The Hollow fiber type LSCF-1928 catalysts prepared with different conditions had different morphologies with finger and sponge like structures. All hollow fiber type catalysts with different pore structure in this study have above 99.9% O_2 conversion at 475 ^oC.This results indicated that hollow fiber type LSCF catalyst promised toremove the minor component O_2 in LFG by dioxygen reaction for near future advanced clean energytechnology.

ACKNOWLEDGMENTS

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