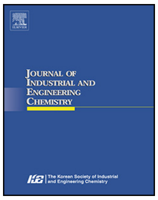
Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Catalytic deoxygen reaction of landfill gas (LFG) at intermediate temperature: The case study of perovskite-type $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ catalysts (LSCF)

Jung Ryoel Kim[a], Eun Ju Kim[b], Edoardo Magnone[b], Jung Hoon Park[b,*]

[a] *Pressure Sensitive Adhesive 1 Team, Aekyung Chemical Co., Ltd, Daejeon 34108, Republic of Korea*
[b] *Department of Chemical and Biochemical Engineering, Dongguk University, Seoul 04620, Republic of Korea*

ARTICLE INFO

Article history:
Received 12 September 2016
Received in revised form 3 November 2016
Accepted 22 November 2016
Available online xxx

Keywords:
Perovskite oxides
Catalyst
Landfill gas
Oxygen removal
Methane oxidation

ABSTRACT

Recently, some perovskite-type oxides with general formula $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ ($0.2 < Sr_x < 0.7$) were found to have reasonable catalytic activity and stability for the deoxygen reaction of landfill gas (LFG) at intermediate temperature. This study selects $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF) at high Sr_x content ($Sr_x = 0.9$) as a case study to investigate the effects of O_2 content on methane oxidation reaction to remove oxygen from the LFG with two compositions characterized by low (1%) and high (2%) O_2 content. The complete oxygen conversion performance (100%) during methane oxidation was found at 425–450 °C and it was maintained throughout the duration of a long-term experiment (100 h).

Introduction

The atmospheric concentration of greenhouse gas (GHG) is increasing continuously day by day as a result of the combustion of fossil fuels. In response to this trend, considerable research has been conducted on the emission and absorption of GHG [1]. Landfill gas (LFG) is one of the largest sources of GHG emissions containing the CH_4 (35–60%) [2] as a major constituent and this is why it can be also considered a kind of renewable resources [3]. In addition to CH_4, the other gases are CO_2 (30–50%), N_2 (2–10%), O_2 (0.1–2%) and trace of other gases like for example ammonia, hydrosulfide, and siloxanes [4–6]. Researches to reduce GHG from LFG were carried out in the way of CO_2 reforming, which use LFG as one of energy sources [5]. Generally, the purity of methane should be at least 98% when using biogas as an energy source [5,6]. Therefore, it is necessary to purify and remove impurities in the gas.

Among other contents, oxygen can cause a degradative corrosion process of all metal part in compressor materials, pipeline and engines [7]. In order to avoid these potential complications, the maximum permitted oxygen concentrations were set between 0.03 and 0.1 mol% in many different countries [8]. Thus, it is necessary to remove oxygen from the captured LFG with the aim of safe transportation and reuse it as a source of energy [9].

To achieve a deoxygenated LFG output from landfill, several techniques are available such as adsorption [10], cryogenics [11], membrane [12], etc. In this context, it is necessary to develop a new strategy to selectively remove the oxygen from captured LFG by a catalytic process in a straightforward low-cost procedure with new advanced catalysts [13].

In this regard, it can be cited that the catalytic activity of Y and Fe co-doped $SrTiO_3$ perovskites for the methane oxidation reaction begins to occur at about 750 °C and it is predominant at a temperature higher than 800 °C [14]. In addition, in the work described by Yoon et al. [14], the catalytic activity increased as the iron content in the $Y_{0.08}Sr_{0.92}Fe_xTi_{1-x}O_{3-d}$ was increased from $x = 0.0$ to $x = 0.4$ and this fact can be easily explained in terms that the “oxygen vacancy concentration is increased with increasing iron content in the perovskite lattice since Fe^{3+} substitution for Ti^{4+} produces oxygen vacancies for charge compensation” [14]. Previous work has also proposed the perovskite-type oxides with general formula $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ with a low-intermediate Sr_x content ($0.2 < Sr_x < 0.7$) over the homogeneous rhombohedral-orthorhombic crystal structure range as advanced catalysts for deoxygen of LFG at the intermediate temperature [15]. More in details, we already reported in Ref. [15] that the oxygen uptake capacities of the selected composition of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$

---

* Corresponding author.
E-mail address: pjhoon@dongguk.edu (J.H. Park).

http://dx.doi.org/10.1016/j.jiec.2016.11.034

Please cite this article in press as: J.R. Kim, et al., Catalytic deoxygen reaction of landfill gas (LFG) at intermediate temperature: The case study of perovskite-type $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ catalysts (LSCF), J. Ind. Eng. Chem. (2016), http://dx.doi.org/10.1016/j.jiec.2016.11.034

perovskite-based catalytic materials ($0.2 < Sr_x < 0.7$) is generally inversely proportional to the catalytic deoxygen process and then the highly favorable catalytic deoxidation was obtained with $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ catalysts characterized by a low Sr_x dopant content ($Sr_x = 0.2$) with a conversion of 50% at about 400 °C and 100% at 500 °C.

In this paper, we extend our previous work in investigating the performance of different $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ sample ($0.2 < Sr_x < 0.7$) [15] to higher Sr_x content ($Sr_x = 0.9$) in LFG type. The main idea of this work is to obtain additional depth information in order to improve the overall catalytic deoxygen performance of the LFG on a $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ sample (LSCF) characterized by high contents in Sr_x ($Sr_x = 0.9$) by an increasing of oxygen vacancy concentration (d) since the Sr^{2+} substitution for La^{3+} in the perovskite lattice produces oxygen vacancies for charge compensation on the substitutional $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ solid solution. As a result, it is expected that a large amount of Sr^{2+} substitution produced not only a structural transition from orthorhombic/rhombohedral ($Sr < 6$) [15] to cubic ($Sr > 0.8$), which was reported by Tai et al. [26], but also increased oxygen vacancies leading to recombination of the charge balance [14,15,26]. Without forgetting the price associated to the material, these two facts together can certainly have crucial impact in terms of catalytic activity of $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ material towards the deoxygen reaction of landfill gas (LFG).

Based on results selected from the literature reviewed, Noble metal (such as Rhodium [16], Palladium [17–19] and Platinum [19,23]) and transition metal (such as Cu [20], Cobalt [20,21]) catalysts were already used for the partial or complete oxidation of CH_4. Table 1 shows some experimental results obtained from the literature on the subject [14–24]. As given in Table 1, most of the catalysts are used for the combustion of emitted gas from the natural gas vehicle (NGV) and for producing of synthesis gas. In addition, we can be noted that generally the O_2 content in the initial gas mixture with CH_4 is an important factor that can determine whether the partial [14,16,24] or total [15,17–22] oxidation reaction is predominant.

In this connection, we investigated the total deoxidation catalytic process of LFG by the LSCF catalyst with high Sr_x content ($Sr_x = 0.9$) where the total oxidation reaction would be illustrated [16] as the following equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

which does not need any additional purification processes because CO and H_2 are not generated by the partial oxidation process of CH_4 as follows:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad (2)$$

From a chemical point of view, these reactions can be considered also as the total reduction reaction of O_2 – the minor component of an LFG mixture – where the CH_4 is the reducing agent.

In conclusion, we focused on developing an advanced catalytic deoxygen process which uses high Sr-doped LSCF catalysts ($Sr_x = 0.9$) to eliminate completely all trace of O_2 from common LFG by a total oxidation process of CH_4 (see Eq. (1)). The ability for oxygen removal was investigated by catalytic oxidation with two LFG compositions characterized by low (1%) and high (2%) O_2 content. In the last section of this work, the performance stability and long-term test (100 h) of LSCF catalysts under selected conditions was investigated.

Experimental

Characterization of LSCF

We used a perovskite-type oxide with nominally general formula $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ with a high Sr_x content ($Sr_x = 0.9$) from Kceracell. Powder X-ray diffraction (XRD) was used to study the crystal phase of the as-received LSCF and ex-situ samples before and after catalytic activity measurements and performance stability test. XRD analysis was performed on a Rigaku D/Max 2200-Ultimaplus diffractometer with Cu Kα radiation ($\lambda = 1.54041$ Å). Data were collected from $2\theta = 20°$ to 80° with a step size of 0.02° at room temperature. Scanning electron microscopy (SEM, HITACHI S-4800) analyses were performed to measure the particle morphology and size of LSCF before and after catalytic activity measurements and performance stability test. In the same way, thermogravimetric analysis (TGA, TA instrument SDT Q600) was conducted in order to measure the thermal weight loss of the LSCF powder at high temperature before and after the experiment. TGA was conducted in air at a flow rate of 100 ml/min. BET surface area was measured and calculated from the BET plot by nitrogen adsorption at −196 °C using Micromeritics ASAP 2420.

Catalytic activity measurements

Fig. 1 shows a schematic diagram of the catalytic reactor for catalytic deoxygen process of the LFG. Briefly, the catalytic reactor consists of a 20 mm inside diameter quartz tube collocated in the middle of a controlled horizontal tubular furnace [15]. About 4 g of LSCF powder was packed into a quartz tube and it was fixed with

Table 1
Methane and oxygen conversion (%) rate of some representative catalysts as reported in literature.

Catalyst	Feed composition (vol.%)	Oxidation	Temp. (°C)[a]	Conversion (%)	Ref.
$Y_{0.08}Sr_{0.92}Fe_xTi_{1-x}O_3$	2% CH_4, 1% O_2 (Ar balance)	Partial	900	63[b]	[14]
$La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$[c]	50% CH_4, 40% CO_2, 2% O_2, 8% N_2	Total	500	100[d]	[15]
Rh-Co/MgO	4% CH_4, 2% O_2 (N_2 balance)	Partial	700	54–76[e]	[16]
Pd/CeO_2	0.5% CH_4, 1% O_2 (He balance)	Total	425	100[b]	[17]
Pd/CeO_2-Al_2O_3	0.5% CH_4, 1% O_2 (He balance)	Total	380	40[b]	[18]
Pd-Pt	1.5% CH_4, 6% O_2 (He balance)	Total	550	100[b]	[19]
CuO	1.5% CH_4, 6% O_2 (He balance)	Total	500	39[b]	[20]
CoO_x	0.5% CH_4, 1.5% O_2, 5% water (Ar balance)	Total	351	20[b]	[20]
CoMn	0.5% CH_4, 1.5% O_2, 5% H_2O (Ar balance)	Total	500	83-86[b]	[21]
$LaMnO_3$	1% CH_4 in air	Total	500	100[b]	[22]
Pt-Rh	52.4% CH_4, 33.6% CO_2, 2.3% O_2 in raw LFG	Total-partial	385	100[d]	[23]
Rh/MgO	4% CH_4, 2% O_2 (N_2 balance)	Partial	700	73[e]	[24]
			Mean = 566	Mean = 81.2–83.7	

[a] Temperature (°C) of the reactor.
[b] Methane conversion (%) by combustion of emission gas.
[c] $0.2 < Sr_x < 0.7$.
[d] Oxygen conversion (%) in LFG.
[e] Methane conversion (%) by partial oxidation to synthesis gas.

Please cite this article in press as: J.R. Kim, et al., Catalytic deoxygen reaction of landfill gas (LFG) at intermediate temperature: The case study of perovskite-type $La_{0.1}Sr_{0.9}Co_{0.2}Fe_{0.8}O_{3-d}$ catalysts (LSCF), J. Ind. Eng. Chem. (2016), http://dx.doi.org/10.1016/j.jiec.2016.11.034