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A study on the feasibility of the catalytic methane oxidation for landfill gas deoxygen treatment

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HIGHLIGHTS

- Oxygen in landfill gas can be removed by catalytic oxidation process.
- Bimetallic Pt–Rh/γ-Al_2O_3 catalyst is suitable for the deoxygen of LFG.
- The temperature for the deoxygen reaction is lower than 460 °C.
- The deoxygen reaction is fastly started-up, and can self-operate without extra heat.
- The catalyst employed can work under wide range of operating conditions.

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ABSTRACT

When landfill gas (LFG) is upgraded as an alternative natural gas or vehicle fuel, in addition to the separation of carbon dioxide, several components such as water vapor, hydrogen sulfide (H_2S), oxygen (O_2) and siloxanes are also need to be eliminated to meet the demands of the corresponding standards. Among these minor components higher content of O_2 would cause some operation problems of the engine combustion equipment that are designed to use natural gas as the fuel. Therefore the oxygen content in upgraded LFG should be strictly controlled to meet the limitation of the corresponding standards. It is difficult to separate O_2 from LFG through conventional technologies. In order to find an effective method to accomplish this work, a deoxygen treatment by which O_2 was removed through the catalytic oxidation of methane was experimentally studied in this paper. In the test, bimetallic Pt–Rh/γ-Al_2O_3 coated on the metallic honeycomb monolith was employed as the catalyst and the compressed raw LFG or the decarbonized LFG at 5.0 bar were used as the feed gas. Results showed that after the catalytic deoxygen reaction was started-up, 100% of deoxygen conversion could be obtained in short time and keep on stably without extra heat supplied. The deoxygen process could be carried out under wide range of operating conditions (gas hourly space velocity up to $1.0 \times 10^5\ h^{-1}$, O_2 content attaining 2.6 vol.%), and the reaction was easier to be started-up for the decarbonized LFG than the raw LFG. Besides, a small amount of gaseous methanol or ethanol mixed into LFG was found to promote the deoxygen reaction remarkably, which might be useful in some special conditions such as cold start. In conclusion, this technique was proved to be promising for the removal of O_2 in the LFG upgrading treatment.

1. Introduction

Landfill gas (LFG) is a kind of important greenhouse gas and renewable energy as it contains large amount of methane. Due to the characteristics of high energy potential, LFG has been widely utilized to generate electricity and heat through combustion in gas engines and boilers. Upgrading LFG to extend its applications, such as a source of vehicle fuel or injecting it into the natural gas grid, attracts an increasing interest in recent years [1,2].

The main components of LFG are methane (CH_4, 40%–60%) and carbon dioxide (CO_2, 35%–50%). In addition, small amounts of nitrogen (N_2), oxygen (O_2), hydrogen sulfide (H_2S) and hundreds of trace components such as siloxanes, hydrocarbons, and halogenated compounds also exist in LFG. The purpose of upgrading LFG is to increase the calorific value of the fuel through separating CO_2 from LFG, and therefore the upgraded LFG could be utilized as an

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alternative natural gas. Various chemical and/or physical methods for LFG or biogas upgrading such as solution absorption (physical and chemical), pressure swing adsorption (PSA), cryogenic, and membrane separation were investigated extensively [3–7] and some of these technologies have been commercialized. Some harmful trace components like water vapor, H_2S, and siloxanes, also need to be removed for upgrading LFG. Several researches were performed on this aspect [4,8].

Small amounts of O_2 and N_2 were frequently detected in LFG because of air incursion into the gas collection system during the process of LFG extraction. Generally the concentration of O_2 monitored in the raw LFG is in the range of 0.5–3.0%. In China, according to the Standards of Compressed Natural Gas as Vehicle Fuel (GB 18047-2000), released by the National Technique and Quality Control Bureau, the high heat value (HHV) of the fuel should be higher than 31.4 MJ/Nm^3, while the contents of total sulfur (S), H_2S, CO_2 and O_2 should be no more than 200 mg/Nm^3, 15 mg/Nm^3 3.0% and 0.5% respectively [9]. Oxygen content determines the air–fuel ratio of the combustion process. If the oxygen content in gas fuel is higher than the requirement, it would cause some engine's operation problems such as difficult to start-up, sudden shut down, low combustion efficiency, and so on due to the inappropriate air–fuel ratio. Therefore in order to meet the standards for LFG to be used as an alternative natural gas or vehicle fuel, the oxygen in LFG should be reduced.

Compared with CO_2, O_2 is much more difficult to be separated from LFG through conventional methods such as absorption, adsorption and membrane separation, thus preventing air from leaking into the LFG by carefully monitoring the gas extraction operation was more preferred [4]. Reducing vacuum in the gas extraction wells during the process of gas extraction can alleviate air leaking into the LFG, however the amount of the collected LFG will also reduce, as smaller extraction vacuum hampers the well's gas extraction performance. Therefore, from the viewpoint of engineering practice, controlling O_2 content through the reduction of vacuum in the gas extraction wells is not cost-effective.

To our knowledge almost no researches have been reported on solving the problem of higher O_2 concentration in LFG upgrading process. Since the main component of LFG is CH_4, which can be oxidized by O_2 through combustion to produce CO_2 or CO under different conditions, thus the minor component O_2 in LFG might be eliminated through the oxidation of CH_4 under appropriate conditions.

In order to achieve CH_4 emission abatement, catalytic oxidation of CH_4 by O_2 has been studied by many research groups [10–14], in which noble metals including palladium, platinum and rhodium were generally employed as the active components of the catalysts and exhibited good catalytic performance on the CH_4 oxidation under lean CH_4 conditions [15]. From the previous research reports, the catalytic CH_4 oxidation could be started-up at temperature about 350–450 °C, and up to 100% of CH_4 conversion could be achieved under higher temperature (normally above 500 °C) [11]. Several reactions (Eqs. (1)–(6)) [12,16–19] may occur during the process of the catalytic oxidation of CH_4. According to these equations, the main products of the catalytic CH_4 oxidation would be CO_2, H_2O, H_2, and CO.

$$\text{Complete oxidation}: CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H^\circ = -803\ \text{kJ/mol} \tag{1}$$

$$\text{Partial oxidation (POX)}: CH_4 + 0.5O_2 \rightarrow CO + 2H_2, \quad \Delta H^\circ = -36\ \text{kJ/mol} \tag{2}$$

$$\text{Steam reforming (SRM)}: CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H^\circ = +206.15\ \text{kJ/mol} \tag{3}$$

$$CO_2\ \text{reforming}: CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^\circ = +247.4\ \text{kJ/mol} \tag{4}$$

$$\text{Water Gas Shift (WGS)}: CO + H_2O \rightarrow H_2 + CO_2, \quad \Delta H^\circ = -41.2\ \text{kJ/mol} \tag{5}$$

$$\text{Reverse Water Gas Shift}: CO_2 + H_2 \rightarrow H_2O + CO, \quad \Delta H^\circ = 34.3\ \text{kJ/mol} \tag{6}$$

In contrast with the above mentioned researches which intended to eliminate small amount of CH_4 under lean CH_4 condition, this work aimed at removing the minor component O_2 in LFG (so-called deoxygen) by means of catalytic oxidation method under rich CH_4 condition. The objective of this study was to determine the feasibility of the catalytic oxidation of CH_4 using the small amount of O_2 in LFG as the oxidant under rich CH_4 condition and then attain the removal of O_2. In this work, a catalyst of bimetallic Pt–Rh/γ-Al_2O_3 coated on a metallic honeycomb monolith was prepared in laboratory and it was used to study the catalytic reactions. The experiments were carried out on a pilot test instrument. The temperature of the inlet and the outlet gas as well as the main components and their contents in the inlet and outlet gas during the reaction process were monitored. In this paper, the characteristics of the catalytic deoxygen reaction was discussed firstly through analyzing a typical deoxygen conversion curve of the decarbonized LFG. Secondly, the type of the catalytic deoxygen reaction was determined based on the data of the main gas components between the inlet and outlet gas and their content variations of twenty-three times of sampling. Moreover, the factors that affect the catalytic deoxygen performance was discussed. Finally, the feasibility for the practical application of the catalytic deoxygen method was analyzed.

2. Material and methods

2.1. Catalyst preparation

Bimetallic Pt–Rh/γ-Al_2O_3 coated on a metallic honeycomb monolith with a hole density of 100 cpsi (cells per square inch) was used as the catalyst in this work. The monolith is a diameter of 50 mm and length of 50 mm cylinder. The catalyst was prepared through several steps. At first 20 g γ-Al_2O_3 was impregnated with aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and $RhCl_3{\cdot}nH_2O$, in which the loadings of Pt and Rh on the γ-Al_2O_3 were 3.0 wt.% and 0.6 wt.% respectively. After the mixture was dried at 120 °C for 2 h and calcined at 580 °C for another 2 h, it was then wet milled with deionized water for 20 h. Slurry of the catalyst was finally coated inside the metallic honeycomb monolith. The dry weight of the coated catalyst was about 15.8 g.

2.2. Experimental trials

A diagrammatic sketch of the setup used for the conduction of the experiments is shown in Fig. 1. The monolith impregnated with catalyst was covered with 100 mm thickness of ceramic fiber to keep adiabatic. It was welded and connected into the pipe system. An electrical preheater was adopted to heat up the inlet gas during cold start, and a water cooler was used to cool down the outlet gas. An organic solvent purge tank was selectively used for blowing small amount of gaseous methanol or ethanol into the LFG. Gas pressure in the system was controlled by the pressure regulating valve.

As it is shown in Fig. 1, the raw or the decarbonized LFG could be switched to be fed into the experimental system. The raw LFG