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# The role of carbon deposition on precious metal catalyst activity during dry reforming of biogas

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**Abstract**

A preliminary investigation into the dry reforming (synthesis gas production) of landfill gas (LFG) was performed using precious metal catalysts. Thermogravimetric analysis work was performed on the dry reforming reaction over 0.5% Pt/γ-$Al_2O_3$ catalysts. Variables such as reforming temperature, $CO_2$ concentration, and the effect of pre-reduction have been studied. It was found that reforming at 900 °C with pre-reduction gave the most $H_2$ production for reactant gas concentrations similar to LFG. However, at this high temperature there was significant weight gain measured. EDX analysis and follow up oxidation tests confirmed that it was due to carbon deposition on the catalyst surface. Yet, this weight gain, up to 24% in some cases, did not coincide with a decrease in catalyst activity as was the case for the lower temperature tests. One possible mechanism for this is the onset of the carbon gasification (Boudouard) reaction at high temperatures. For increased $CO_2$ concentrations, the activity of the catalyst at high temperatures was maintained (high production of syngas) despite significant carbon deposition.
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*Keywords:* Greenhouse gas reforming; Carbon formation; TGA

## 1. Introduction

As global energy demands increase, more consideration will be given to the future of energy supply. With the ultimate goal to develop a hydrogen economy, attention has recently been given to $H_2$ production from all sources. This has led to the increasing study of the dry reforming of methane focusing on the development of catalysts which exhibit high activity and stability [1,2]. One emergent area in particular is the use of biogas produced from anaerobic decomposition of organic material. This biogas typically contains equal amounts of $CH_4$ and $CO_2$, which if reformed properly can provide a renewable source of hydrogen essentially from waste [3]. Landfills are currently the largest source of this biogas in that they decompose municipal solid wastes anaerobically and landfill gas to energy (LFGTE) projects that directly combust the LFG are being implemented.

Landfills are also the largest source of U.S. methane emissions and they have emitted approximately 37 to 57 million tonnes of methane or 13–20% of the total U.S. methane emissions in 2006 [5,6]. Municipal Solid Waste (MSW) landfills generate 93% of U.S. landfill methane emissions. Over 2500 landfills currently operate in the U.S. [7] The 1996 Clean Air Act requires the reduction of methane emissions from landfills. Landfill methane emissions can be reduced through methane recovery and use projects (e.g. landfill gas to energy – LFGE), as well as flaring. Currently, only about 330 U.S. landfills have methane utilization projects out of 600 candidate landfills [5]. The recovered methane is used as on-site fuel to generate electricity, or sold to energy end-users [5,8,9].

The $CO_2$ and $CH_4$ from the landfills are ideal candidates for reforming reactions that yield either; (i) synthesis gas (CO and $H_2$) [10], to be used directly to enhance the combustion performance of various systems or (ii) high value products such as ethylene [10,11]. These reforming reactions are endothermic and as such require substantial amounts of energy to drive them. The implementation of the right catalytic reactor will overcome this contraint by combining exothermic reactions and selectivity to provide the necessary energy and promote the desired reforming reactions. The ideal scenario then would be to operate the reforming reactions in an autothermal mode where heat released, via exothermic reactions, provides the necessary energy to drive the desired endothermic reactions. One way to do this is to mix the $CO_2/CH_4$ feed with air or oxygen resulting in a fuel-rich

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