Applied Catalysis B: Environmental 94 (2010) 125–133

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Auto-thermal and dry reforming of landfill gas over a Rh/γAl_2O_3 monolith catalyst

McKenzie P. Kohn [a], Marco J. Castaldi [a,*], Robert J. Farrauto [a,b]

[a] *Earth and Environmental Engineering Department, Columbia University, 500 West 120th Street, New York, NY 10027, USA*
[b] *BASF Catalysts, 25 Middlesex Turnpike, Iselin, NJ 08830, USA*

ARTICLE INFO

Article history:
Received 22 July 2009
Received in revised form 26 October 2009
Accepted 30 October 2009
Available online 10 November 2009

Keywords:
Auto-thermal reforming
Dry reforming
Landfill gas
Rhodium monolith catalyst

ABSTRACT

Auto-thermal and dry reforming of methane and carbon dioxide mixtures was investigated experimentally at temperatures between 300 °C and 800 °C at atmospheric pressures using a Rh/γAl_2O_3 monolith catalyst. CH_4:CO_2 ratios of 1:1 and 1.4:1 were tested. The Rh catalyst reached equilibrium conversions of CH_4 and CO_2 to H_2 and CO for both CH_4:CO_2 ratios. Equilibrium analysis shows that carbon formation is likely for dry reforming but not for auto-thermal reforming. Experimentally, carbon formation was seen after long-term exposure to 1.4:1 CH_4:CO_2 ratios without oxygen, but the catalyst has shown the ability to be regenerated in air. Auto-thermal tests, with and without external heat input, operating at an equivalence ratio of 4.3 (O_2:CH_4 = 0.46) and maintaining the CH_4:CO_2 ratio of either 1:1 or 1.4:1, did not show signs of carbon formation or deactivation. ATR experiments resulted in H_2:CO ratios between 1.0 and 2.0 that can be tuned depending on the monolith temperature, beneficial in the case of downstream Fischer–Tropsch processes. For the auto-thermal experiments, theoretical reaction extents were calculated based on experimental data and showed two primary regimes in catalyst operation: a CH_4 combustion and partial oxidation regime, and reforming and water–gas shift regime.

1. Introduction

It is estimated that of the 413 million tons of municipal solid waste (MSW) generated per year in the United States, 64.5% is landfilled [1]. The biomass that makes up 67% of that municipal solid waste anaerobically decomposes in landfills to CH_4 and CO_2. A characteristic landfill gas (LFG) is composed of 45–55% CH_4, 30–40% CO_2, 10–15% N_2, 0–5% O_2, and other trace compounds, but the composition varies depending on the type of waste and the age of the landfill. Approximately 50–100 Nm^3 of methane is generated per ton of MSW landfilled per year, and continues to be generated for at least 50 years after a landfill closes. Currently less than 10% of this is captured and used for energy [2]. This is likely to change as the demand for energy increases making complete and efficient utilization of LFG more important.

As of 2008 there were 565 LFG to energy conversion projects that generate electricity or deliver LFG for direct heating [3] with others being considered to produce liquid natural gas [4]. A challenge of using landfill gas for energy is its low heating value that can result in low flame stability and when combusted can produce more emissions, such as NOx, CO, and unburned hydrocarbons compared to high quality fuels. In addition, the variable composition (CH_4:CO_2 ratios of 1.4:1 to 1:1) makes it difficult to develop a process that yields a consistent output. In these cases, the methane is flared and released as CO_2. One solution to these issues is to catalytically dry reform a portion of the LFG to syngas for more robust combustion. The syngas can also be converted to liquid fuels using Fischer–Tropsch or to a H_2 rich stream using water–gas shift for hydrogen applications.

Dry reforming is a very endothermic reaction and has a high propensity for coke production, especially on base metal catalysts such as Ni [5–7]. Carbon formation on a catalyst can result from either thermodynamically or kinetically governed processes or a combination of both. From a global perspective there are three primary reactions that drive the formation of carbon; CO disproportionation (1), CO reduction (2), and CH_4 decomposition (3) [7]. The dry reforming reaction is also shown below (4). Initially the CH_4 decomposition reaction is kinetically controlled, since there is no H_2 or C in the influent. If carbon is formed during this reaction, as the concentration of carbon increases, the CO disproportionation reverse reaction will initiate to produce CO, which then can react with H_2 to yield C and H_2O via the reduction reaction. The formation of carbon becomes favored as the reaction proceeds due the production of H_2 and CO.

CO disproportionation:

$$2CO \leftrightharpoons CO_2 + C \quad \Delta H = -172\,kJ\,mol^{-1} \tag{1}$$

---

* Corresponding author.
E-mail address: mc2352@columbia.edu (M.J. Castaldi).

0926-3373/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2009.10.029