



# Biogas reforming for syngas production: The effect of methyl chloride



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## ABSTRACT

Biogas is a mixture of primarily methane and carbon dioxide produced from the anaerobic microbial digestion of biomass. A 4% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated for its ability to reform biogas in the presence of a chloride impurity, specifically CH<sub>3</sub>Cl that is often found in biogas systems. The conditions tested included temperatures between 350 °C and 700 °C with CH<sub>3</sub>Cl concentrations between 0 and 200 ppm at atmospheric pressure and 1050 h<sup>-1</sup> WHSV. It was determined that in the dry reforming reaction CH<sub>3</sub>Cl reacts with the alumina support to produce surface chloride which increases the surface acidity and reversibly poisons the reverse water–gas shift reaction. For example, with the addition of 50 ppm CH<sub>3</sub>Cl the H<sub>2</sub>/CO ratio increased by 40% at 350 °C and by 2% at 700 °C. All changes were reversible upon removal of CH<sub>3</sub>Cl from the feed. Furthermore, less surface chloride was observed using XPS at 700 °C compared to 400 °C, and the effect on selectivity decreased with CH<sub>3</sub>Cl concentrations less than 50 ppm. Therefore the degree of chloride poisoning is directly proportional to CH<sub>3</sub>Cl concentration and inversely proportional to temperature.

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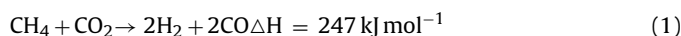
## 1. Introduction

Biogas is a mixture of methane and carbon dioxide produced from the anaerobic microbial digestion of biomass. The gas is often produced in landfills, agricultural operations, and in wastewater treatment plants. Biogas from landfills alone is the second largest source of anthropogenic methane emissions in the United States, producing 13.5 billion m<sup>3</sup> of methane per year [1]. In the U.S. only 18% of landfill gas is used for energy [2,3] because the high CO<sub>2</sub> content decreases the heating value and flame stability of the gas mixture. This leads to increased CO, NO<sub>x</sub>, and unburned hydrocarbon emissions when the gas is combusted in an engine, turbine, or boiler compared to pure CH<sub>4</sub> or natural gas [4]. Therefore biogas is often flared without extracting any of the latent chemical energy.

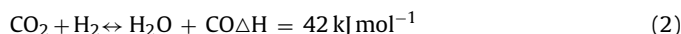
Catalytic dry reforming of biogas (Eq. (1)) has the potential to fully utilize the energy contained in the biogas by converting both the CH<sub>4</sub> and CO<sub>2</sub> into H<sub>2</sub> and CO, or syngas [5]. Syngas is valuable because it can be used as a combustion enhancer due to its high reactivity [4], which decreases the emissions associated with combusting the biogas, or as a precursor for liquid fuels or fuel cells [6]. Dry reforming is usually accompanied by the reverse water–gas shift reaction (Eq. (2)) that decreases the H<sub>2</sub>/CO ratio to a value slightly less than one in the temperature range of 400–800 °C. In

this work a Rh/Al<sub>2</sub>O<sub>3</sub> catalyst is used because it is less susceptible to carbon formation during dry reforming which can deactivate the catalyst compared to base metals such as nickel [7].

### Dry Reforming



### Reverse Water–Gas Shift

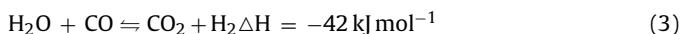


One problem with catalytically reforming biogas is the trace amounts of sulfur and chlorinated compounds present that could potentially poison the catalyst. The effect of sulfur compounds on reforming catalysts has been widely studied because sulfur is commonly present in oil and its derivatives such as gasoline [6]. Chlorocarbons are not as widely studied although they are present in biogas [8,9], as well as in the gasification and combustion products of biomass, coal, and municipal solid waste [10–13] in amounts similar to sulfur compounds (10–50 ppm) [8]. The chlorocarbons originate from the natural presence of chlorinated compounds in organic material that are released during decomposition, gasification or combustion of organic material. Therefore as the production of bio-derived fuels increases, the effect of chlorocarbons on reforming catalysts will become more important. CH<sub>3</sub>Cl, the simplest chlorocarbon and most abundant atmospheric halocarbon, is used as the chlorocarbon surrogate in this work to investigate the effect of 10–50 ppm of a chlorinated compound on the activity and selectivity of the dry reforming reaction over the Rh/γAl<sub>2</sub>O<sub>3</sub> catalyst.

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While the effect of  $\text{CH}_3\text{Cl}$  on the dry reforming reaction has not been previously studied, steam reforming of various chlorocarbons over base and precious metal catalysts supported on  $\gamma\text{Al}_2\text{O}_3$  has been studied. Richardson et al. [14–22] found that for a variety of chlorocarbons, chloride adsorption on the catalyst poisons the forward water–gas shift reaction, Eq. (3), but not the chlorocarbon steam reforming activity, shown for  $\text{CH}_3\text{Cl}$  in Eq. (4).

#### Water–Gas Shift



#### $\text{CH}_3\text{Cl}$ Steam Reforming:



The most active catalysts for the steam reforming reaction were Rh, Pt, and Pd followed by Cu, Re, Ir, Ru, Ni, and then Co, in decreasing activity. On the precious metal catalysts carbon formation occurred to some extent but was not a major cause for activity loss. Experiments with both  $\text{CH}_3\text{Cl}$  and  $\text{CH}_4$  suggested that the two species may compete for reforming sites and that  $\text{CH}_3\text{Cl}$  reacts preferentially. On all catalysts supported on alumina, a loss in water–gas shift activity was observed via an increase in CO and a decrease in  $\text{CO}_2$  at temperatures lower than  $700^\circ\text{C}$  [17]. Chlorocarbon steam reforming experiments on a Pt/ $\text{ZrO}_2$  catalyst, however, did not exhibit water–gas shift poisoning, while the chlorocarbon reforming activity remained high and close to equilibrium [22], showing a sensitivity to the catalyst support.

After the chlorocarbon steam reforming experiments, regeneration of the water gas shift (WGS) activity using  $\text{H}_2\text{O}$  was possible. To explain these results, it was suggested that chloride replaces alumina hydroxyl sites that are in equilibrium with steam. By replacing these alumina hydroxyl (OH) sites, chloride poisons the WGS reaction which is also dependent on these OH sites. The replacement of alumina hydroxyl groups by chloride is supported by other work showing that on a working alumina catalyst, in which a mixture of Lewis acid, Brønsted acid, and basic sites exist, HCl can dissociate on the catalytic acid–base pairs to form Al–Cl and  $\text{H}_2\text{O}$  [23]. The net reaction is a replacement of one alumina hydroxyl group with a chloride as shown in Eq. (5) [24,25]. The net reaction clarifies the role of the  $\text{H}_2\text{O}$  gas concentration for keeping the alumina surface free of chloride.



The replacement of a hydroxyl group, which in most configurations is basic, increases the acidity of the alumina [26]. The presence of the chloride also polarizes the lattice of hydroxyl groups and weakens the remaining O–H bonds [26,27], increasing the Brønsted acidity of the alumina. The effect of chloride adsorption on support acidity is well known in the field of naphtha reforming in which chlorocarbons are supplied to maintain the acidity of a Pt/ $\text{Al}_2\text{O}_3$  or Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst [6]. The increased support acidity affects the water gas shift reaction which is dependent on the basicity of the support, originating primarily from the alumina hydroxyl (OH) groups, to produce the necessary formate or carbonate intermediates [28–33] to proceed in either the forward or reverse direction.

## 2. Experimental methods

### 2.1. Catalyst preparation

A 4% Rh/ $\gamma\text{Al}_2\text{O}_3$  catalyst, obtained from BASF Catalysts, was used for all of the experimental work presented here. The catalyst was prepared using a rhodium nitrate solution so that any chloride present on the catalyst originated from the reaction conditions and not the preparation technique. The powder catalyst was prepared by ball milling the impregnated catalyst to an average

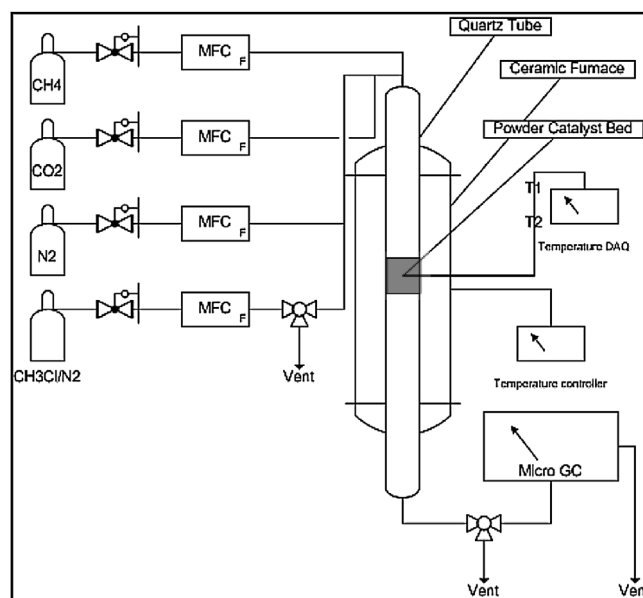


Fig. 1. Schematic of flow-through reactor apparatus (not to scale).

particle size of  $10 \mu\text{m}$ . The density of the 4% Rh/ $\text{Al}_2\text{O}_3$  powder was  $0.84 \text{ g/cm}^3$ . The catalyst was calcined in air at  $725^\circ\text{C}$ . The BET specific surface area of the calcined catalyst powder was  $110 \text{ m}^2/\text{g}$ , measured using a Quantachrome Nova 2200e. The dispersion of the Rh metal was 40%, measured using CO chemisorption with a thermo-gravimetric analyzer (Netzsch, STA 409 PC Luxx) assuming a 1:1 CO:Rh adsorption ratio. The mean particle size, calculated using the 40% dispersion value, was  $2.7 \text{ nm}$ , assuming Rh atom surface area =  $7.58 \text{ \AA}^2$  and Rh density =  $12.4 \text{ g/cm}^3$  [34].

### 2.2. Flow-through reactor

Flow-through reactor experiments were performed in a quartz reactor (Fig. 1) operated at 1 atm pressure and temperatures between  $350^\circ\text{C}$  and  $700^\circ\text{C}$ . The quartz tube had an inner diameter of  $1.905 \text{ cm}$  and length of  $30.5 \text{ cm}$ .  $0.15 \text{ g}$  of 4% Rh/ $\text{Al}_2\text{O}_3$  powder composed the catalyst bed, resulting in a bed size of  $1.905 \text{ cm}$  diameter and  $0.09 \text{ cm}$  length. The flow rate of the reactant gases was  $2100 \text{ ml}\cdot\text{min}^{-1}$ , or  $2.6 \text{ g}\cdot\text{min}^{-1}$ , resulting in a weight hourly space velocity (WHSV) of  $1050 \text{ h}^{-1}$  or a gas hourly space velocity (GHSV) of  $705,600 \text{ h}^{-1}$  in order to reduce diffusion and mass transfer effects. UHP  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$  (Techair) were used to simulate a landfill gas. A mixture of  $1000 \text{ ppm}$   $\text{CH}_3\text{Cl}$  in  $\text{N}_2$  (Techair) was used to introduce  $\text{CH}_3\text{Cl}$ . The mass flow rate of each inlet gas into the reactor was controlled with mass flow controllers (Aalborg, GFC17). A tube furnace was controlled with a temperature controller (Omega, CN9000A Series) and K-type thermocouples (Omega, KMTIN Series). One thermocouple was placed upstream of the catalyst bed to measure the gas preheat temperature, and another thermocouple was placed in the catalyst bed to measure the reaction temperature.

Flow-through reactor tests were performed by exposing the 4% Rh/ $\text{Al}_2\text{O}_3$  powder catalyst to a target mixture of 5.5%  $\text{CH}_4$ , 7%  $\text{CO}_2$  in a balance of  $\text{N}_2$  until the reactor temperature and conversion stabilized. A mixture of  $1000 \text{ ppm}$   $\text{CH}_3\text{Cl}$  in  $\text{N}_2$  was used to introduce  $\text{CH}_3\text{Cl}$ . The final  $\text{CH}_3\text{Cl}$  concentration was 10, 25, or  $50 \text{ ppm}$   $\text{CH}_3\text{Cl}$ , depending on the experiment. The  $\text{CH}_3\text{Cl}$  was introduced for 1 h.  $\text{CH}_3\text{Cl}$  was then removed and the test continued to run for at least 1 h with the initial gas mixture. When  $\text{CH}_3\text{Cl}$  was introduced, the  $\text{N}_2$  flow rate was reduced to maintain a constant flow rate.

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