Effect of co-fed CH_4 in the conversion of CO_2 in biogas to synthetic natural gas over a Ru/CeZrO₂ catalyst Robby Wampler¹, Mayra P. Almeida², Raimundo Rabelo-Neto², Fabio B. Noronha², Gary Jacobs¹

ABSTRACT

Biogas is a mixture of mostly carbon dioxide (~25%-50%) and methane (~50%-75%) and often contains other trace compounds such as nitrogen, hydrogen sulfide, hydrogen, ammonia, oxygen, and carbon monoxide. This gaseous mixture is produced through the process of anerobic digestion, which occurs as microorganisms break down organic compounds (often wastewater, municipal waste, or biomass). CH₄ in biogas can be utilized as a fuel yielding 5.5–7 kWh m–3. CO_2 methanation (CO_2 + 4H₂ \rightarrow CH₄ + $2H_2O$) on biogas increases the energy that can be produced by combustion. Herein, we utilized a Ru/CeZrO₂ catalyst for CO₂ hydrogenation to CH_4 . In-situ infrared spectroscopy experiments support a mechanism occurring at the Ru-CeZrO₂ interface, where reduced defects are present in CeZrO₂. This proposed cycle involves adsorption of CO₂ to make surface carbonates, hydrogenation of surface carbonate to formate, conversion of formate to CO and -OH, and the hydrogenation of CO on Ru nanoparticles to CH_4 . Using a feed mixture of 17% CH_4 , 17% CO_2 , and balance H₂, and a similar H₂/CO₂ ratio mixture without co-fed CH₄, an autocatalytic effect of methane was detected, such that co-fed methane resulted in an increase in its rate of formation. This led to the hypothesis that methane present in the feed facilitated formation of Ru surface carbide, increasing methanation. Support for Ru carbide formation came from temperature programmed hydrogenation of catalysts post-reaction.

INTRODUCTION

Due to growing concern regarding environmental problems stemming from high greenhouse gas emissions from fossil fuel combustion, the demand for renewable fuels is rapidly increasing. As such, there is growing demand for bio-methane due to its various applications in electricity production, heat and steam generation, and vehicular fuel. One promising method of producing bio-methane comes from biogas, a mixture of primarily CO_2 and CH₄ produced from the anerobic digestion process that occurs as microorganisms break down biomass. It is estimated that biogas will play a major role in the rapidly growing market for renewable energy sources and, as such, the demand for biogas will rapidly increase over the coming years. Since biogas can be produced from feedstocks containing waste products such as natural fertilizers, plant biomass, sewage, and municipal waste, it is estimated that the utilization of the resulting bio-methane will lead to a 20% reduction in the impact on global warming compared to methane produced from traditional sources. The goal of this research is to increase the amount of energy that can be recovered from biogas mixtures by increasing its CH_4 content through the methanation of CO_2 using Ru/CeZrO₂ catalysts.

METHODS

CO₂ methanation reactions were carried out in a fixed-bed tubular reactor at 300°C and atmospheric pressure. Both $CO_2/H_2/CH_4$ and $CO_2/H_2/He$ reactant mixtures were tested to explore the effect of co-fed CH₄ on activity and selectivity. In separate temperature-stepped experiments using the two different feed mixtures, in-situ DRIFTS spectroscopy was used to determine the nature of the surface species, potentially intermediates, present on the catalyst surface, as well as their response to increasing temperature. Following these experiments, temperature programmed hydrogenation was used to characterize the used catalysts. TCD and mass spectroscopy allowed for the observation of H_2 uptake and CH_4 formation by the reaction of hydrogen with Ru carbide on the catalyst surface.

Department of Chemical Engineering ¹CEID, The University of Texas at San Antonio ²INT, Rio de Janeiro, Brazil

RESULTS

| Catalysts | Weight (mg) | Feed | Conversion of CO ₂ (%) | Reaction rate for formation of CH ₄ (mol/mol _{Ru} .s) | Reaction rate for formation of CO (mol/mol _{Ru} .s) | CH ₄ Selectivity (%) | CO Selectivity (%) |
|-----------------------|----------------|--|--------------------------------------|--|---|---------------------------------------|--------------------------|
| Ru/CeZrO ₂ | 65 | He:CO ₂ :H ₂ | 3.9 | 0.0208 | 0.0703 | 22.3 | 77.7 |
| Ru/CeZrO ₂ | 65 | CH ₄ :CO ₂ :H ₂ | 3.8 | 0.0456 | 0.0422 | 52.1 | 47.9 |

Figure 1. Reaction rate, CH_4 and CO selectivities for hydrogenation of CO_2 a 300°C over Ru/CeZrO₂ after reduction at 500°C

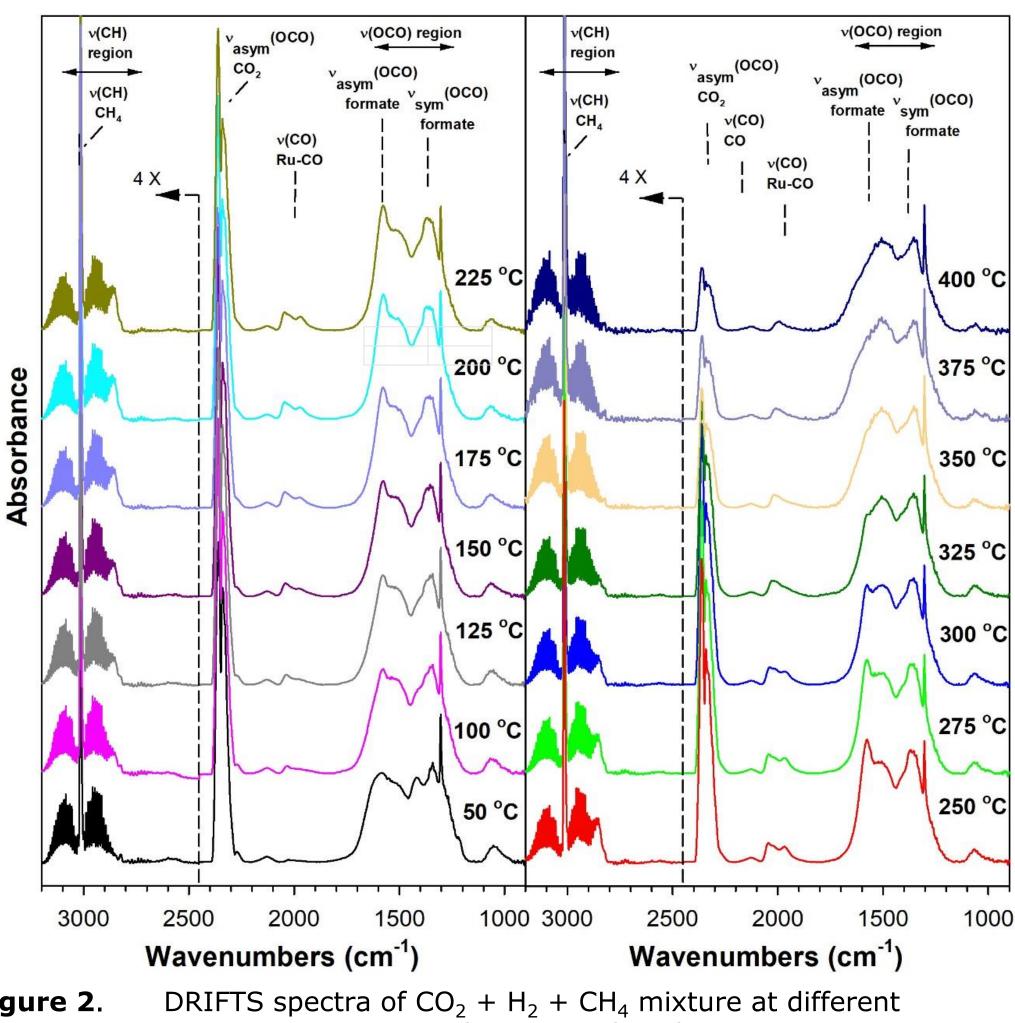
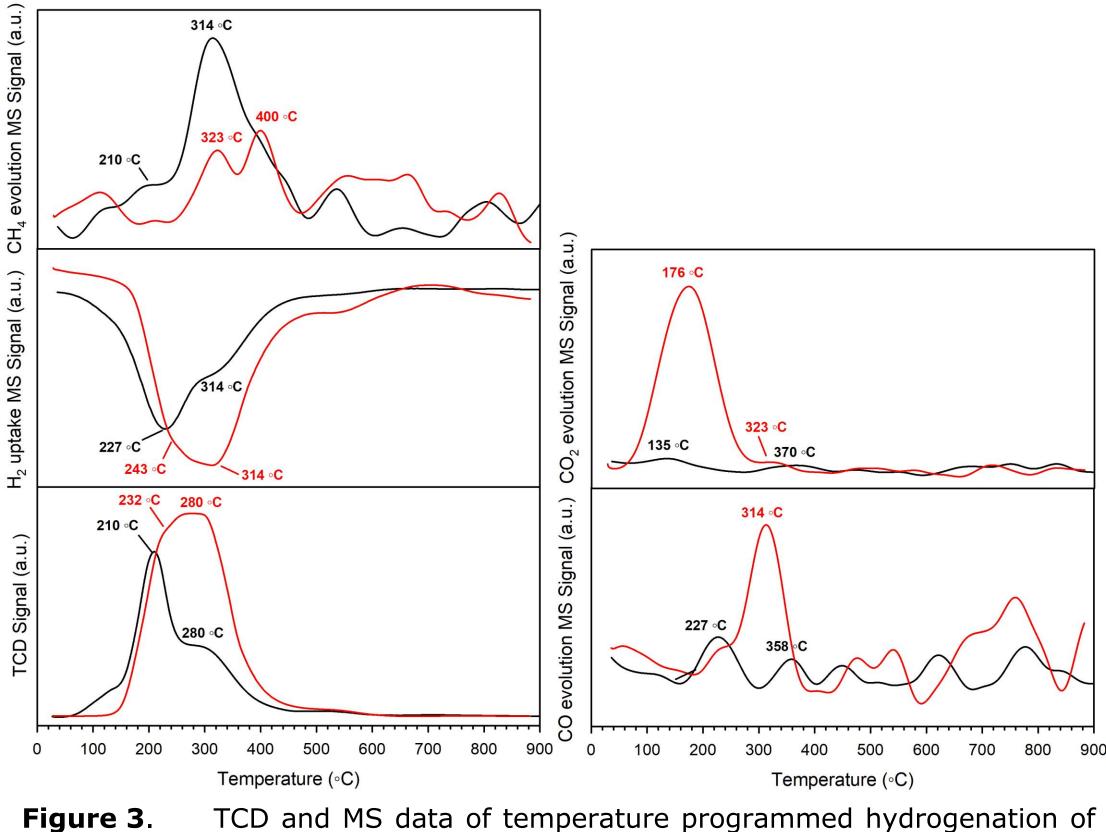


Figure 2.

temperatures over Ru/CeZrO₂ reduced at 500°C.



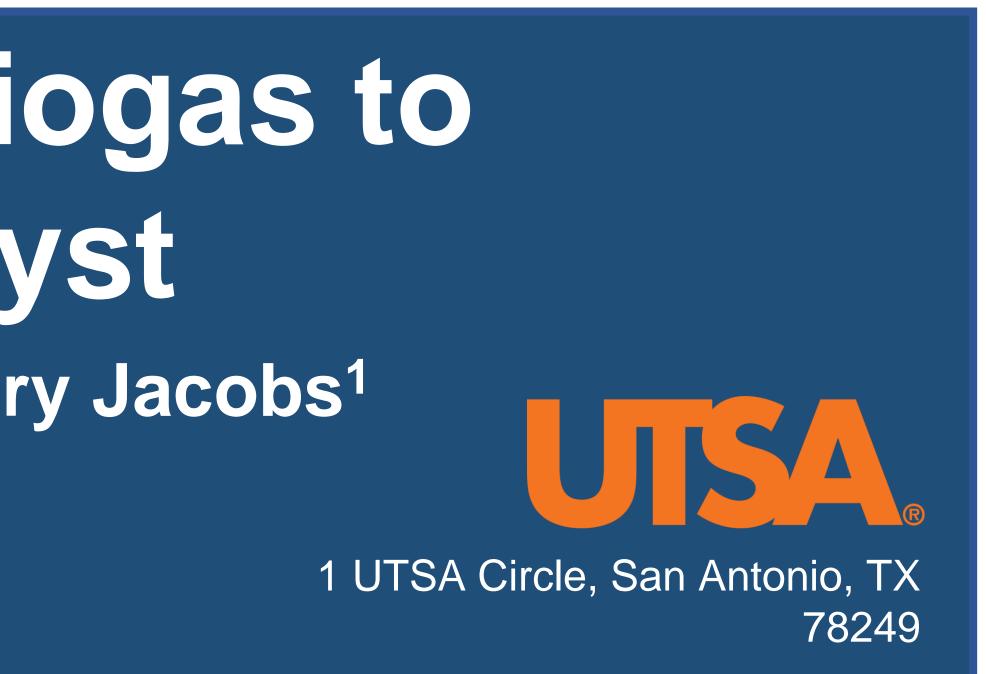
Ru/CeZrO₂. The black line represents the catalyst reacted with co-fed methane and the red line represents the catalyst reacted without co-fed methane.

The tabulated data includes the rates of formation and selectivity of CO and CH₄ for both feed mixtures. While both reactions resulted in similar conversions of CO_2 , the reaction in which feed methane was added resulted in a significantly greater rate of formation and selectivity of CH_4 . This data has led to two claims: first, methanation of CO_2 occurs in two steps involving a partial reduction in which the CO_2 is reduced to CO and then a second reduction in which the CO is hydrogenated to CH_4 , and second, the methane in the feed mixture has an autocatalytic effect with the Ru/CeZrO₂. Looking at the DRIFTS spectra, the key band is the formate C-H stretching vibration at 2850 cm⁻¹. This band is weak, indicating that it is an absorbed species without rotational structure. The formate intensity increases up to about 225°C then decreases, which supports the claim that surface formate acts as an intermediate in converting CO₂ to CO, which is consistent with the proposed two-step methanation mechanism. Additionally, the v(CH) band at 2850 cm⁻¹ increases in intensity as temperature increases, which is inversely related to the intensity of the $v(CO_2)$ band at 2349 cm⁻¹. This is consistent with the proposed overall reaction in which CO_2 is hydrogenated into CH_4 . Additionally, looking at the temperature programmed hydrogenation data of used catalysts, the important spectra is the CH_4 evolution. The black spectra, which represents the catalyst that was reacted with co-fed methane, has a much more intense peak than the catalyst that was not reacted with cofed methane. This peak, in addition to its temperature, suggests that the Ru nanoparticles under co-fed CH₄ were carbided. Also, the catalyst reacted without co-fed methane produced much more intense CO and CO_2 evolution signals. This is likely due to the catalyst having more intermediates on the surface than the catalyst reacted with co-fed CH₄.

The goal of increasing the methane content of biogas mixtures using $Ru/CeZrO_2$ catalyzed methanation of CO_2 was accomplished. In addition, a two-step mechanism of the CO₂ methanation reaction was proposed in which CO_2 is partially reduced to CO via surface formate intermediates before being fully hydrogenated to CH₄. Additionally, an autocatalytic effect of co-fed methane was observed, leading to temperature programmed hydrogenation experiments being performed to support the hypothesis of Ru carbide formation. While the TCD and MS data support this viewpoint, additional experiments are needed to further characterize the used catalysts reacted with co-fed methane.

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RESULTS

CONCLUSION