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Generation of syngas through autothermal partial oxidation of glycerol over $LaMnO_3$- and $LaNiO_3$-coated monoliths

Shih-Kang Liu, Yu-Chuan Lin*

Department of Chemical Engineering and Materials Science, Yuan Ze University, Chungli, Taoyuan 32003, Taiwan

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ABSTRACT

This study presents a side-by-side comparison of $LaMnO_3$ and $LaNiO_3$ perovskites in the autothermal partial oxidation of glycerol to syngas. Pure glycerol and glycerol/water solutions were converted to syngas under adiabatic conditions. The addition of water suppressed glycerol conversion and reaction temperature, but increased H_2 selectivity with the appropriate steam-to-glycerol feed ratio. Catalytic results show that $LaMnO_3$ is more active than $LaNiO_3$ in autothermal partial oxidation because of its combustion-prone nature. In contrast, $LaNiO_3$ produced higher H_2 selectivity than $LaMnO_3$ did. A comparative study of $LaMnO_3$ and $LaNiO_3$ in glycerol steam reforming and water-gas shift was performed as well to reveal how these H_2-production reactions proceed in the oxygen-deficient regime of a catalyst bed. The outcomes indicate that $LaNiO_3$ is more active than $LaMnO_3$ in these two reactions, thereby enhancing H_2 selectivity in a partial oxidation system. Moreover, a 24-h lifetime test of these two perovskites was conducted, showing that $LaMnO_3$ has greater durability.

1. Introduction

Biodiesel is a renewable energy source with the potential to alleviate fossil-fuel dependency, reduce smog-forming and greenhouse gas emissions, and transform waste such as used kitchen grease into valuable products. However, biodiesel synthesis by transesterification inevitably produces glycerol as a byproduct. The glycerol accumulation has caused economic and environmental problems, impeding the development of the biodiesel industry [1].

As stated by Pagliaro and Rossi [2]: "...to expand biodiesel production, it is essential for economical utilization pathways for the glycerol by-product to be developed, either by expanding the existing markets for glycerol, or, better still, by establishing new marketable value-added derivatives." Therefore, researchers have developed various techniques to ease the over-supply of glycerol, e.g., pyrolysis [3], steam reforming [4,5], and aqueous-phase reforming [6,7] of glycerol to hydrogen-rich gases, hydrogenolysis of glycerol to propylene glycol [8], and oxydehydration of glycerol to acrylic acid [9]. Unfortunately, none of these processes has yet been commercialized, possibly because of a limited scale or rate of production.

The partial oxidation of glycerol to syngas under autothermal conditions at millisecond contact times is a promising method for glycerol abatement [10–13]. An adiabatic system can be used to convert viscous and high-boiling-point glycerol to syngas without heat supply, and further achieve orders of magnitude H_2 space time yield [14]. Syngas, a mixture of CO and H_2, is a building block for numerous chemicals [15]. Converting waste glycerol to syngas can likely reduce human dependence on fossil-fuel derived chemicals. For example, a biodiesel plant can use glycerol-derived syngas in methanol synthesis [11]. BioMCN is currently using crude glycerol-derived syngas in methanol production [16]. This renders the autothermal partial oxidation of glycerol an attractive method of syngas generation.

Noble metal catalysts, such as Pt and Rh, are frequently used in the partial oxidation of glycerol [10–12]. However, the high expense of noble metal and thermal sintering through on-stream operations hinder the practical implementation of these catalysts. Our group recently tested $LaMnO_3$ perovskite as a support and an active phase in glycerol partial oxidation, and showed that $LaMnO_3$ perovskite has superior thermal stability and oxidation activity compared with Pt catalysts [13]. This indicates that perovskite is comparable to noble metal catalysts for glycerol partial oxidation in short-contact-time reactors. However, $LaMnO_3$ promotes glycerol combustion, and is inactive in H_2-production reactions such as steam reforming and water-gas shift (WGS). This makes $LaMnO_3$ less favorable than Pt for syngas production. Therefore, exploring effective perovskite for glycerol partial oxidation to syngas is required.

This study extends our previous study of $LaMnO_3$ perovskite [13] to a broader range of conditions, and investigates the effects of heterogeneous and homogeneous chemistries in glycerol

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* Corresponding author. Tel.: +886 3 463 8800x3554; fax: +886 3 455 9373.
E-mail addresses: yclin@saturn.yzu.edu.tw, yclin768@gmail.com (Y.-C. Lin).

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conversion. A side-by-side comparison of two perovskites ($LaMnO_3$ and $LaNiO_3$) was conducted. The Ni-based catalysts are widely used in glycerol steam reforming [14], and using Ni-containing perovskite might have a positive effect in H_2 generation in the oxygen-deficient zone of an autothermal reforming system. Moreover, $LaNiO_3$ is effective in the autothermal reforming of ethanol [17]. These factors led us to choose $LaNiO_3$ as an alternative to $LaMnO_3$ in the autothermal partial oxidation of glycerol.

2. Experimental

2.1. Catalyst preparation

A cordierite (50% SiO_2, 34% Al_2O_3, and 16% MgO) honeycomb monolith was used as the supporting material. The foam density is 20 pores per linear inch (ppi), with a 19-mm in diameter and a 1-cm length. The surface area of the monolith is approximately 0.23 m^2/g. Both $LaMnO_3$- and $LaNiO_3$-coated monoliths were prepared using the active-phase deposition method [13,18]. The monolith was repeatedly submerged in a slurry consisting of γ-Al_2O_3 powder (10 wt%), nitric acid (65%), and pseudoboehmite (10 wt%). After coating approximately 25 wt% of alumina, the monolith was calcined in air at 550 °C for 3 h. Subsequently, 5 wt% La_2O_3 was doped onto the alumina-washcoated monolith as a stabilizer by the wet impregnation of an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$. The treated monolith was then dried at 120 °C overnight and calcined at 800 °C for 3 h in air. Finally, active-phase $LaMnO_3$ or $LaNiO_3$ (20 wt%) was wet-impregnated onto the monolith and calcined at 900 °C for 3 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a Shimadzu Labx XRD-6000 with Cu Kα radiation (0.15418 nm). Scans were performed at a scanning rate of 4°/min over a 20–80° angle range (2θ). The voltage and current were 40 kV and 30 mA, respectively. Temperature-programmed reduction (TPR) was carried out by a Micromeritics apparatus model (Autochem II 2920) with a thermal conductivity detector (TCD). Approximately 100 mg of the sample was consumed per trial. The sample was dehydrated at 150 °C in an N_2 stream (30 mL/min) for 30 min prior to each test. Dehydrated samples were then reduced in a 10% H_2/Ar (30 mL/min) stream at a 5 °C/min heating rate to 900 °C. Surface morphologies and compositions were surveyed using scanning electron microscopy (SEM, JEOL JSM-5600) equipped with an energy dispersive spectrometer (EDS, Oxford INCA Energy 350). The SEM accelerating voltage was 10 kV. The scanned areas were approximately 0.12 mm × 0.09 mm. Both as-prepared and post-reaction catalysts were characterized by XRD, TPR, and SEM-EDS.

2.3. Reactor design and product analysis

The reactor used for the autothermal partial oxidation of glycerol in this study had a design similar to that of Rennard et al. [11,12], and has been described in detail elsewhere [13]. Glycerol or a glycerol/water solution was directed into the system by a syringe pump (KD Scientific, KDS-100) at ambient temperature. The glycerol feeding rate was maintained at 0.54 mL/min for both pure glycerol or glycerol/water mixtures. The liquid feed was blended with mixed nitrogen and oxygen (inlet pressure at 50 psi) before entering a nebulizer (Burgener Research, SS-50). The nebulizer sprayed small droplets of the feed directly onto the catalytic zone. The contact times ranged from 16.5 to 43.8 ms for $LaMnO_3$ (915–472 °C) and 18.2–43.7 ms for $LaNiO_3$ (804–474 °C). Table A1 of Appendix A (Supporting Information) detailed experimental conditions. The experiment parameters were set to maintain steady-state autothermal operations. Deactivation was not observed within 3 h for each data point. The catalytic zone consisted of two active phase-coated monoliths on top of a blank foam. Three K-type thermocouples were placed at the front, center, and back of the two monoliths to record reaction temperatures under autothermal conditions. The reactivity of a single monolith was also investigated, and the temperatures of the front and back faces were recorded. Table A2 of Appendix A (Supporting Information) presents the experimental settings. All trials for glycerol partial oxidation were tested adiabatically.

To evaluate the effects of steam reforming and WGS on the autothermal system, these two reactions were tested using conditions (i.e., measured temperature and contact time) similar to those of partial oxidation. For glycerol steam reforming, the reaction temperatures were the same as the back-face temperatures of glycerol partial oxidation over the two catalyst-coated monoliths. WGS was tested from 200 to 600 °C. Both of steam reforming and WGS were performed isothermally, using two catalyst-coated monoliths. Contact times were the same as those of partial oxidation, using pure N_2 as the carrier gas. Tables A3 and A4 of Appendix A (Supporting Information) show detailed experimental parameters. Glycerol partial oxidation, using a single monolith, was tested to determine the catalytic performance when oxygen breakthrough occurred.

The outlet of the reaction system was connected to a cold trap. Condensable exhaust was trapped, and the remaining exhaust was vented to a fume hood. Non-condensable products were collected in gas bags. Trapped species were analyzed using a gas-chromatography-mass spectrometry (HP 5890 II GC with 5972 MSD, DB-5MS capillary column, 60 m × 0.25 mm), and gaseous products were analyzed by a GC TCD/FID equipped with a methanizer (SRI-8610, 13X molecular sieve and silica gel columns) using Ar as the carrier gas. Identified compounds included nitrogen, oxygen, carbon oxides, hydrogen, methane (CH_4), ethylene (C_2H_4), propylene (C_3H_6), formaldehyde (CH_2O), acetaldehyde (C_2H_4O), hydroxyacetone ($C_3H_6O_2$), acrolein (C_3H_4O), pyruvaldehyde ($C_3H_4O_2$), glycerol ($C_3H_6O_3$), benzene (C_6H_6), and toluene (C_7H_8). Nitrogen served as the carrier gas and the internal standard for GC response factors. Molar effluents were quantified to close material balances of C, H, and O atoms, primarily within ±10%. Water was estimated based on oxygen atom balance. Reported data points were recorded in triplicate under steady-state conditions to achieve a 95% confidence interval. Glycerol conversion, product selectivity, and the feed ratio were defined as follows:

$$\text{Glycerol conversion}\,(X_G): \quad \frac{\text{moles of glycerol reacted} \times 100\%}{\text{moles of glycerol injected}}$$

$$\text{Carbon selectivity}\,(S_C): \quad \frac{\text{C atoms in species}\,\alpha \times 100\%}{\text{C atoms in converted glycerol}}$$

$$\text{Hydrogen selectivity}\,(S_H): \quad \frac{\text{H atoms in species}\,\alpha \times 100\%}{\text{H atoms in converted glycerol}}$$

The feed's carbon-to-oxygen ratio (C/O):

$$\frac{\text{C atoms in glycerol}}{\text{O atoms in the feeding } O_2}$$

The feed's steam-to-carbon ratio (S/C):

$$\frac{\text{moles of water in the feed}}{\text{C atoms in glycerol}}$$