Study of the hydrogen production by aqueous phase reforming of glycerol over Ni-based catalysts

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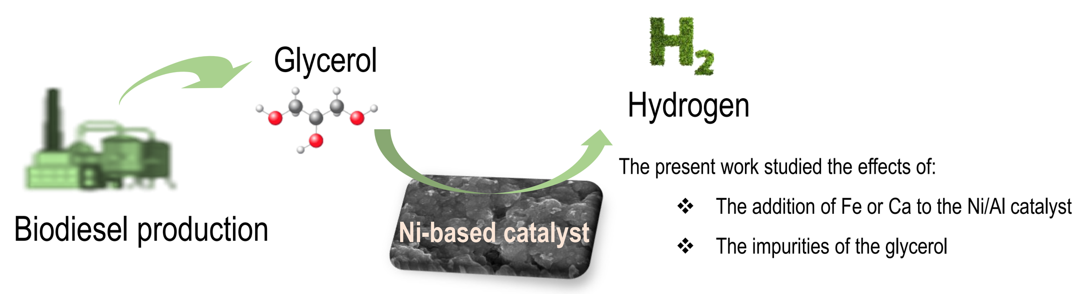
OBJECTIVES



INTRODUCTION

Nowadays, the high production of biodiesel is due to an increase in the environmental crisis caused by the high consumption of fossil fuels in the last decades. The transport sector accounts for around 60 % of global oil consumption and produces one-fifth of global CO_2 emissions. Biodiesel production generates glycerol as a by-product, which could negatively affect its economy. Therefore, several processes have been investigated to valorize glycerol. In this context, **hydrogen production** from **aqueous phase reforming (APR) of glycerol** is a promising method to improve the economic viability of biodiesel industries [1-2].

EXPERIMENTAL

CATALYST PREPARATION

Three different Ni-based catalysts were prepared by the **co-precipitation method** described by Raso et al. [3], keeping the Ni content constant at 28 molar % and changing the molar ratio of Al/Fe or Al/Ca from 1/0 to 3/1 or 13.3/1, respectively. The catalysts were named **Ni/Al, Ni/Al$_3$Fe$_1$, and Ni/Al$_{13.3}$Ca$_1$** and calcined at 500 ºC for 3 h.

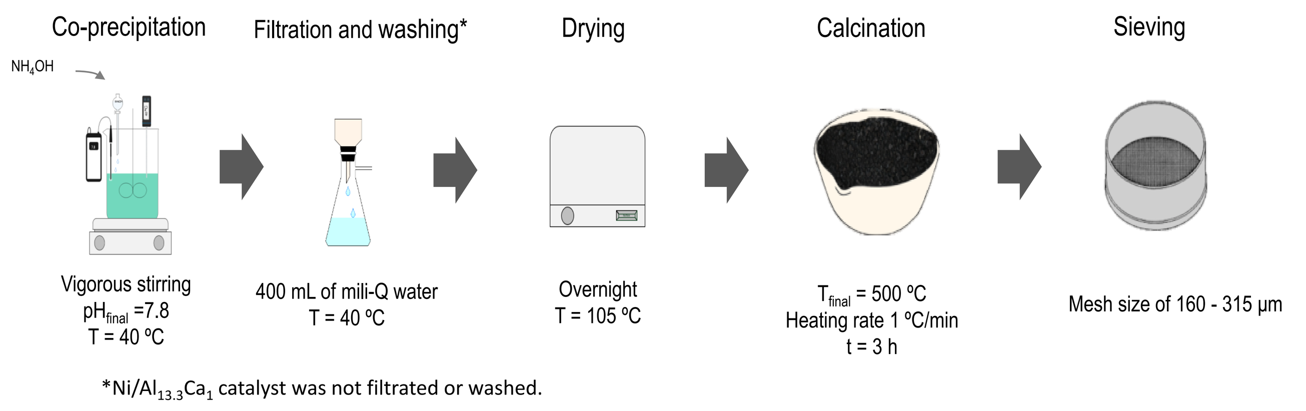


Fig. 1. Schematic diagram of the catalyst preparation.

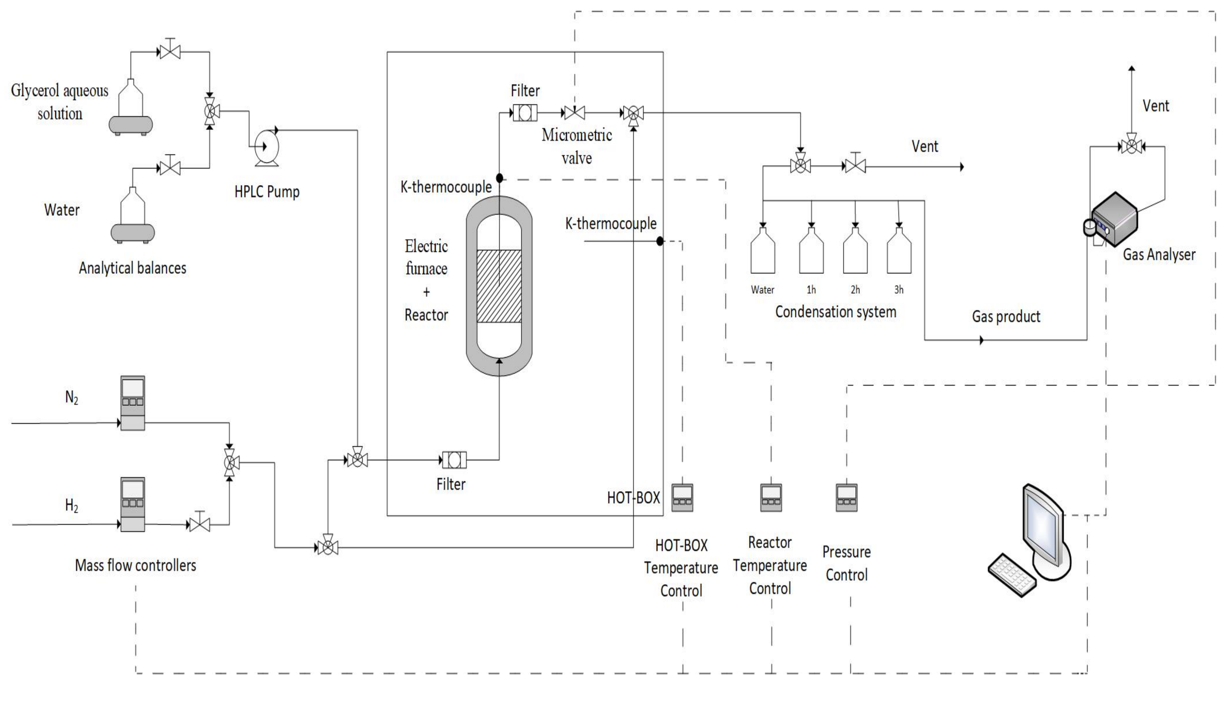


Fig. 2. Schematic diagram of the catalyst performance system [3].

CATALYST PERFORMANCE

Table 1. Experimental conditions.

T (ºC)	P (bar)	F* (wt.%)	W (g_{cat})	Total Flow (mL/min)	t (h)
238	37	5	2	1	3

*: Chemical glycerol (Sigma-Aldrich, purity: 99.5 %) or bio-glycerol (obtained from biodiesel production, purity: 86.1 %).

The gas stream was analyzed online by an Agilent 490 **Micro-GC** equipped with thermal conductivity detectors (TCD). The liquid products were analyzed offline using total organic carbon (**TOC**) equipment.

RESULTS AND DISCUSSION

- Adding Fe or Ca to the Ni/Al catalyst favored the reduction (NiO to Ni) at low temperatures.

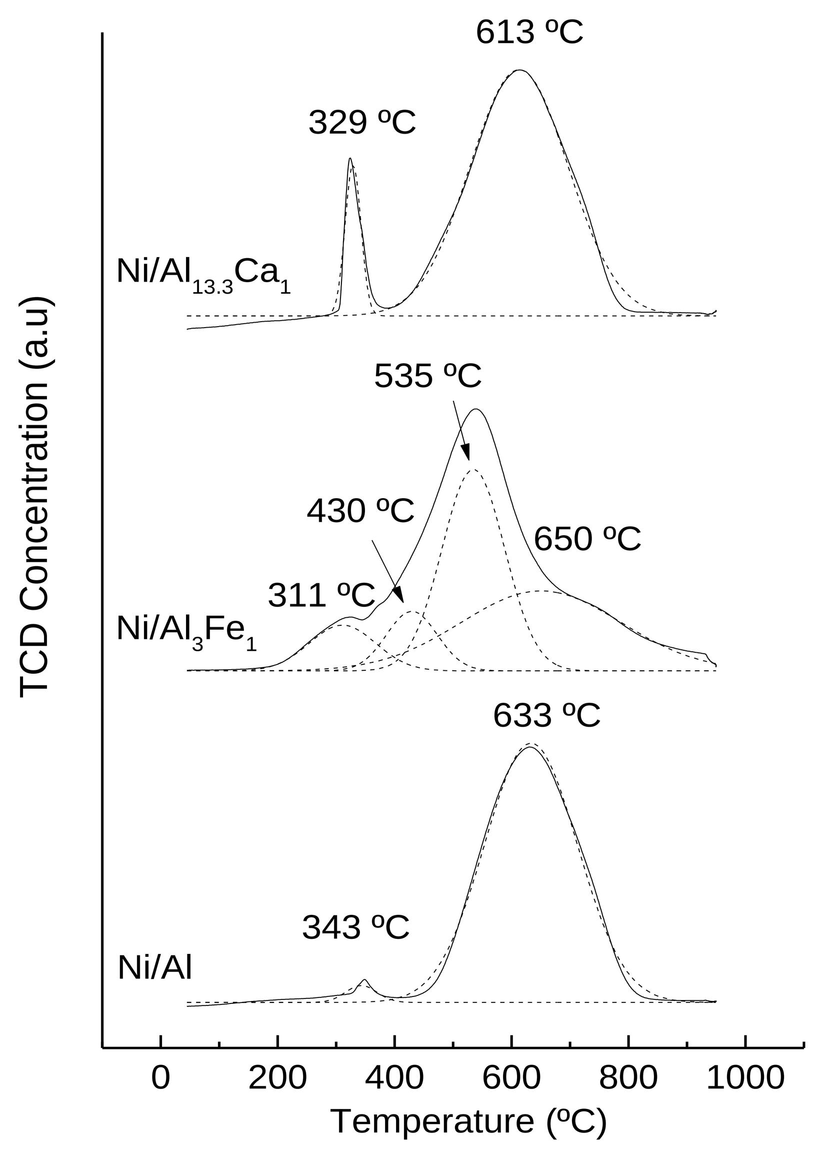


Fig. 3. H_2-TPR profiles of the calcined catalysts.

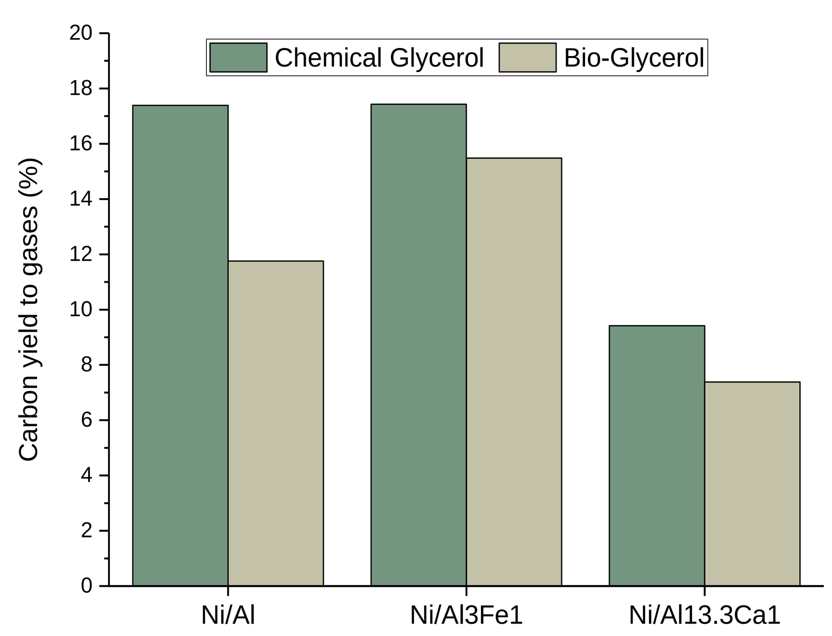


Fig. 4. Carbon yield to gases.

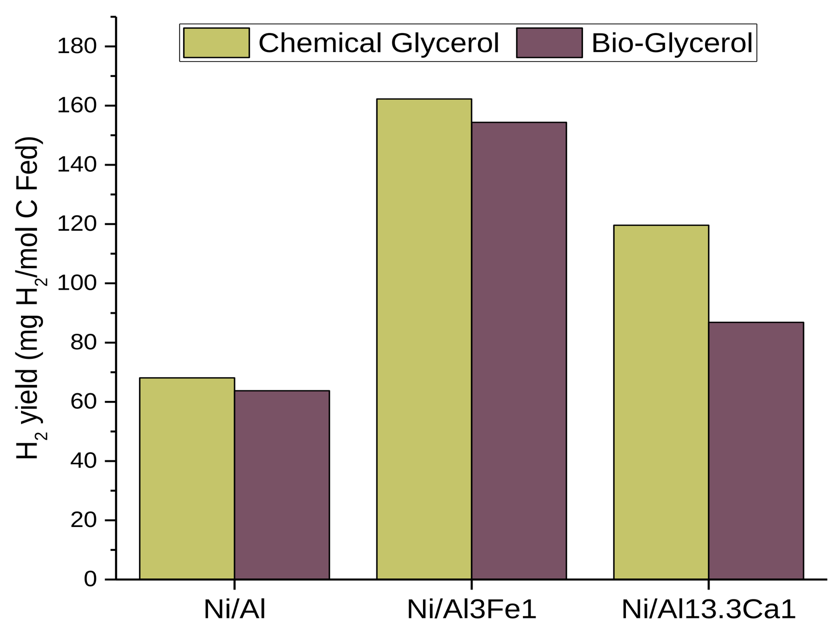


Fig. 5. H_2 yield expressed as mg H_2/mol C fed.

- Gas composition: adding Fe or Ca to the Ni/Al catalyst
  ↑ H_2 and CO_2 ↓ CH_4 ≈ C_2H_6 and C_3H_8 Practically not found CO
- The carbon yield to gas and the H_2 yield were higher for all catalysts when chemical glycerol was fed than when bio-glycerol was provided.
- The Ni/Al$_{13.3}$Ca$_1$ catalyst showed the lowest carbon yield to gas, while the Ni/Al catalyst indicated the lowest H_2 yield.

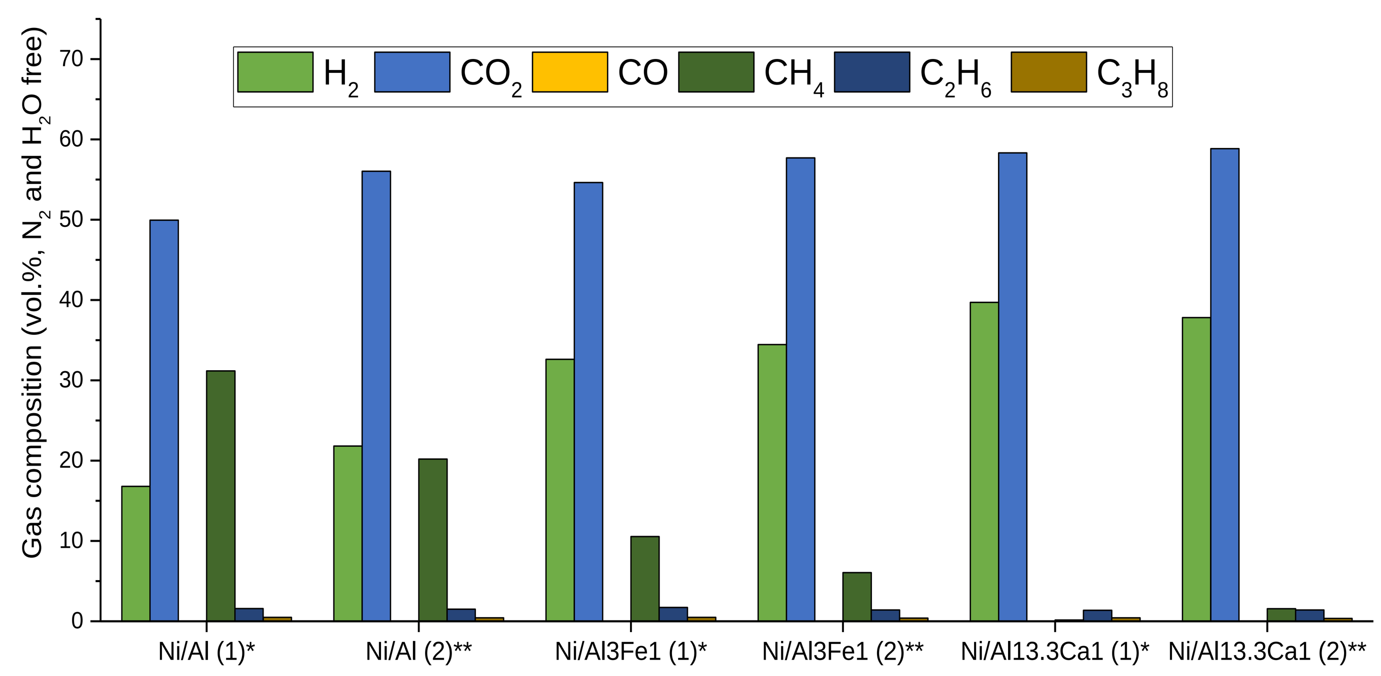


Fig. 6. Gas composition.

*: Chemical glycerol (Sigma-Aldrich, purity: 99.5 %).

**: Bio-glycerol (obtained from biodiesel production, purity: 86.1 %).

CONCLUSIONS

- ❑ Adding Fe or Ca to the Ni/Al catalyst favored the reduction (NiO to Ni) at low temperatures.
- ❑ The chemical composition of the catalyst and glycerol impurities influenced the H_2 production by APR of glycerol.
- ❑ The H_2 yield decreased in the following order: Ni/Al$_3$Fe$_1$ > Ni/Al$_{13.3}$Ca$_1$ > Ni/Al.

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