



Research article

Ruthenium doped nickel-alumina-ceria catalyst in glycerol steam reforming

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ABSTRACT

Crude glycerol excess as a by-product of biodiesel industry has given rise to the need to valorize glycerol, e.g. its conversion to hydrogen by steam reforming. While many studies have been made towards catalyst development and their performance, catalyst selectivity and stability continue to be issues of further investigation. In this work, ruthenium doped nickel-alumina-ceria catalyst has been studied. The catalyst was prepared by wet impregnation method. Characterization was done with BET surface area, SEM, temperature programmed reduction, temperature programmed oxidation and pulse hydrogen chemisorption techniques. Performance test experiments were carried out in a packed bed reactor with aqueous glycerol feed, in water to glycerol mole ratio 12:1, at temperatures 550 °C to 800 °C, weight hourly space velocity of 10 h⁻¹ and atmospheric pressure. It was found that 10Ni-1Ru/Al₂O₃/5CeO₂ catalyst showed superior catalytic performance and stability, compared to 10Ni/Al₂O₃ and 10Ni/Al₂O₃/5CeO₂. Hydrogen selectivity of 88.6% was obtained versus a thermodynamic value of 95.9% at 650 °C. The catalyst was also stable for 24 h on stream. From the kinetic study, overall activation energy was found to be 70.82 kJ/mol and order of reaction with respect to glycerol and steam were 0.31 and 0.52 respectively.

1. Introduction

In view of long term detrimental effects associated with fossil fuel use, recent years have seen increased effort in the search for alternative renewable energy sources. Biodiesel is one of these, being a biodegradable, non-toxic and a near CO₂-neutral option. However a side effect is the production of large amounts of glycerol as by-product. About 10% by weight of the biodiesel produced is glycerol. It is already in surplus and the mismatch between demand and supply is likely to grow with more biodiesel production. Therefore management of the glycerol excess is important and processes to valorize it need development.

Several processes like steam reforming, autothermal reforming, partial oxidation, dry reforming, supercritical water gasification and pyrolysis, can be used to convert glycerol to value added products, namely hydrogen. Among these, steam reforming has the advantage of easy control and not requiring high pressure. However catalysts with high selectivity and stability, and preferably requiring mild process conditions, are needed. Many authors have attempted to develop efficient metallic catalysts with different supports and modifiers [1,2]. Nickel is one of the more studied transition metal catalysts and is reported to have good activity for cleavage of C–C, O–H and C–H bonds. Moreover, it is found to be efficient in catalyzing the water-gas shift

reaction occurring in steam reforming. But it suffers deactivation because of coke deposition and sintering of nickel clusters [3–6]. For improving activity and selectivity, noble metal catalysts such as ruthenium, rhodium, palladium, platinum and iridium [7–11] have been studied. Of these, ruthenium is relatively less costly and displays high catalytic activity. But employing ruthenium or other noble metals alone for catalysis is not economical.

Hence low loadings (up to ~2.5 wt%) of ruthenium on different support materials or bimetallic Ru-doped Ni, Fe, Co on Al₂O₃, Y₂O₃, ceria-zirconia, etc., have been found to be a better option. Ru and Ni have synergistic effect and aid in the self-activation. Alumina support is preferred due to its large surface area and thermal stability whereas ceria is used as a promoter and enhances both metal activities and anti-coking attributes. Hirai and coworkers [7] examined H₂ production by glycerol steam reforming employing ruthenium based catalysts and reported complete conversion of glycerol and 90% hydrogen yield over Ru/Y₂O₃. Adhikari et al. [8] used 2.5 wt% Ru loading in Ru/Al₂O₃ and Ru/CeO₂-Al₂O₃ catalysts and found the latter to be better. Profeti et al. [10] evaluated Ni-Al₂O₃/CeO₂ doped by platinum, palladium, ruthenium and iridium at 700 °C and found more or less similar gas product distribution, H₂ being 55–60%. Kim and Lee [12] studied monometallic 1 wt% Ru as well as bimetallic Ru-Fe, Ru-Co, Ru-Ni on alumina, yttria

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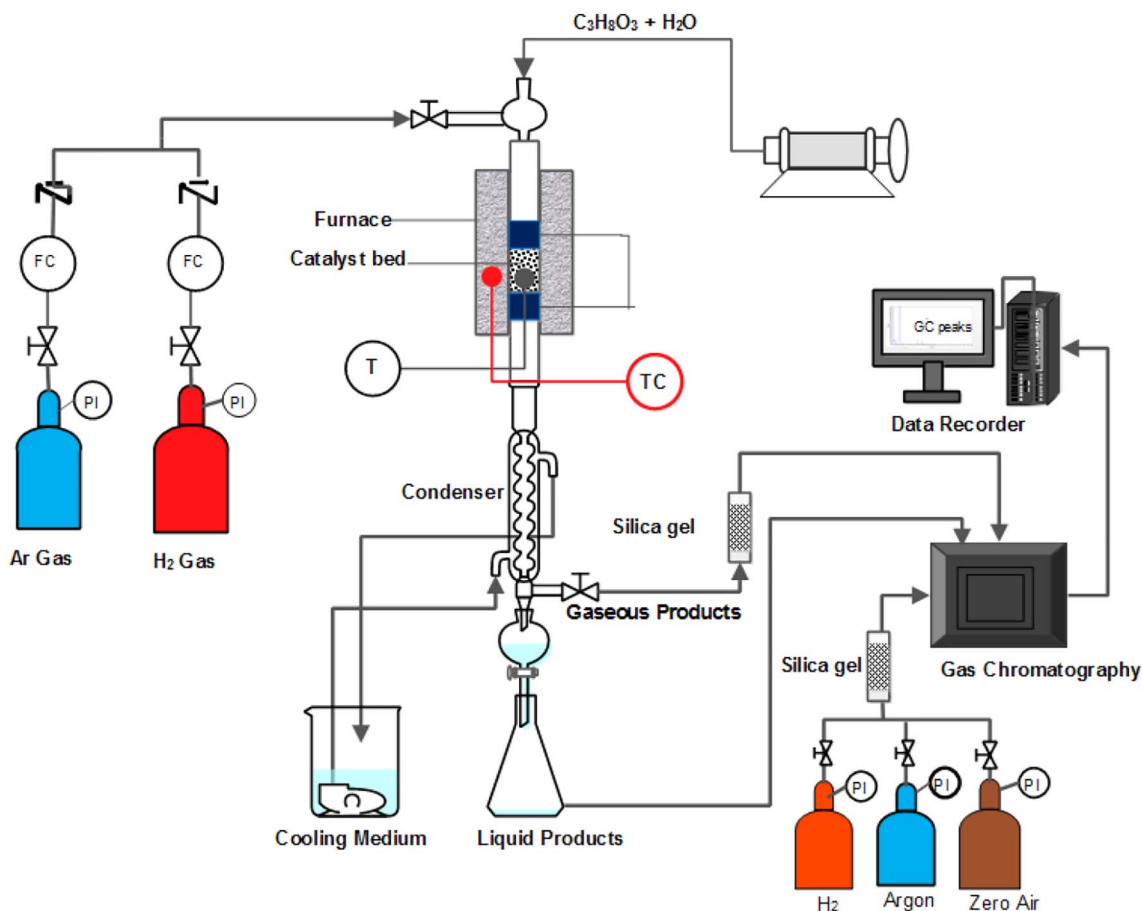


Fig. 1. Laboratory set-up for glycerol steam reforming.

Table 1
BET surface area, pore volume, average pore diameter and dispersion.

Catalysts	BET surface area (m ² /g)	Pore volume (cc/g)	Average pore diameter (Å)	Dispersion (%)
10Ni/Al ₂ O ₃ /5CeO ₂	113	0.51	62	28.1
10Ni-1Ru/Al ₂ O ₃ /5CeO ₂	109	0.50	62	32.4
γ-Al ₂ O ₃	200	0.60	69	Not applicable

and ceria-alumina supports. They observed that the type of support had more effect on conversion and H₂ selectivity. More recently, Martinez et al. [13] examined Ru on CeZr, CeZrCo mixed oxides for glycerol steam reforming and found the latter to favour selectivity and longer activity. Gallegos-Suarez et al. [11] studied Ru supported on different carbon materials such as activated carbon, nanofibers, graphite and carbon nanotubes. Kousi et al. [14] studied modified Ru/Al₂O₃ catalysts (promoted with B₂O₃ or MgO) for glycerol steam reforming. They obtained 92% conversion and 68% H₂ yield with Ru/Al₂O₃ but the modified catalysts were not as good and all three were not very stable.

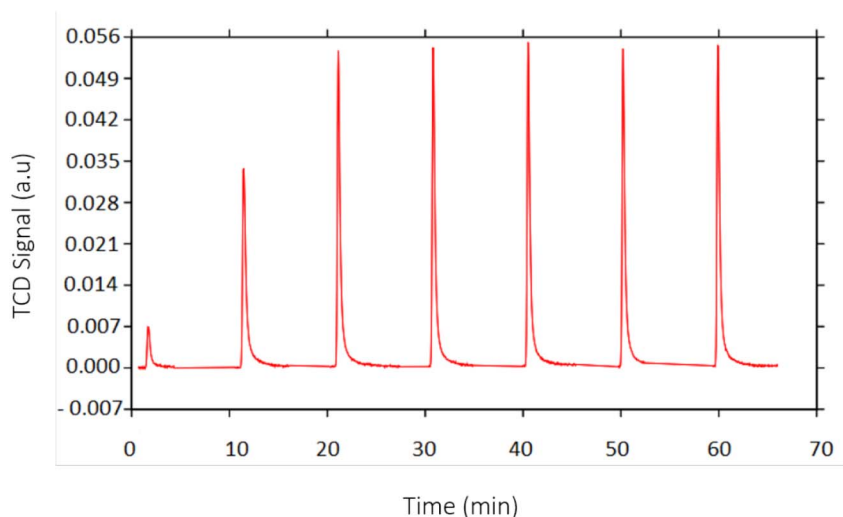


Fig. 2. Hydrogen chemisorption for 10Ni-1Ru/Al₂O₃/5CeO₂.

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