



Comparing nickel and cobalt perovskites for steam reforming of glycerol

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ABSTRACT

Catalytic steam reforming of glycerol, a by-product of biodiesel production, to form hydrogen was carried out over nickel and cobalt generated in-situ *ex* perovskite nano-crystallites, LaNiO₃ and LaCoO₃, respectively. These materials were prepared using a reverse microemulsion. The glycerol conversion over these materials was modelled as a 1st order reaction and has a lower activation energy (28 kJ/mol) over the sample *ex* LaNiO₃ than the glycerol conversion over the sample *ex* LaCoO₃ (40 kJ/mol). The hydrogen selectivity increases with increasing temperature as expected from a thermodynamic analysis and is higher in the glycerol conversion over LaNiO₃ (106.5H-% implying some conversion of water as well) compared to LaCoO₃ (80H-%). The obtained distribution of organic product compounds is rationalized based on the higher rate of C–C bond cleavage relative to the rate of C–O bond cleavage for nickel in comparison to cobalt. It is further noted that cobalt *ex* LaCoO₃ is more stable than nickel *ex* LaNiO₃ possibly due to the lower tendency to form carbon deposition over the former sample.

1. Introduction

The development of the technology utilizing biomass as an energy resource attracts much attention seeing the anticipated peak-oil and the resulting decrease in the fossil fuel supply. This in addition to the growing demand for energy worldwide require new technologies using novel energy carriers. Replacing classical fossil fuels with renewable energy carriers may enforce the development of a circular economy and so limiting the increase in the atmospheric CO₂-levels. Therefore, biodiesel is gradually being accepted as a replacement for petroleum-based diesel [1]. A disadvantage of the introduction of biodiesel is the co-production of crude glycerol during the catalytic transesterification process, which amounts to ca. 10 wt.-% of the amount of biodiesel generated. [2,3].

Glycerol can be converted into hydrogen or hydrogen-rich synthesis gas (syngas) via steam reforming [4–7] resulting in the formation of hydrogen from a (partial) renewable source in an indirect manner. Hydrogen is widely used in the chemical and petroleum industries as well as a promising clean energy for electrical power generation in fuel cell devices [8]. Furthermore, syngas (CO + H₂) is a useful feedstock for industrial process, such as hydroformylation, methanol synthesis and even the Fischer–Tropsch synthesis.

Glycerol steam reforming can be directed to yield selectively H₂, CO, CO₂ and CH₄ [9–14]. The purity of the products depends on reaction condition, such as temperature, pressure and steam to carbon

ratio. Adhikari et al. [15,16] showed that hydrogen production in glycerol steam reforming is thermodynamically favoured at high temperature (> 600 °C) and low pressure using a high steam to glycerol ratio. Low temperatures and low steam to glycerol ratios will thermodynamically favour methane and carbon, products whose formation is associated with a reduced hydrogen formation.

Catalyst are not only selected based on activity and selectivity considerations. Economic factors come into play as well. Noble metals such as Pt, Pd, Ru, and Rh are often used for steam reforming of glycerol, but noble metals are rather expensive and typically scarce [17–20]. Hence, cobalt and nickel-based catalytic systems, that inhibit coke formation [21–28], have been explored. Perovskite type oxides (ABO₃) with a well-defined structure can be an alternative to metal-based precursors, where nano-sized materials have shown to have an increased activity and a reduced tendency for coke formation [25–27]. The use of nickel-containing perovskite-derived catalysts for glycerol steam reforming has been shown to give a more homogeneous distribution of the catalytically active metal within the catalyst [26,27] and smaller nickel particles [26] resulting in an improved activity and selectivity. Here, we compare cobalt and nickel based perovskites, LaCoO₃ and LaNiO₃, as a starting material for glycerol steam reforming, in particular focusing on the variability of product distribution during this reaction taking cognizance of chemical equilibrium considerations and the presence of the homogeneous reactions.

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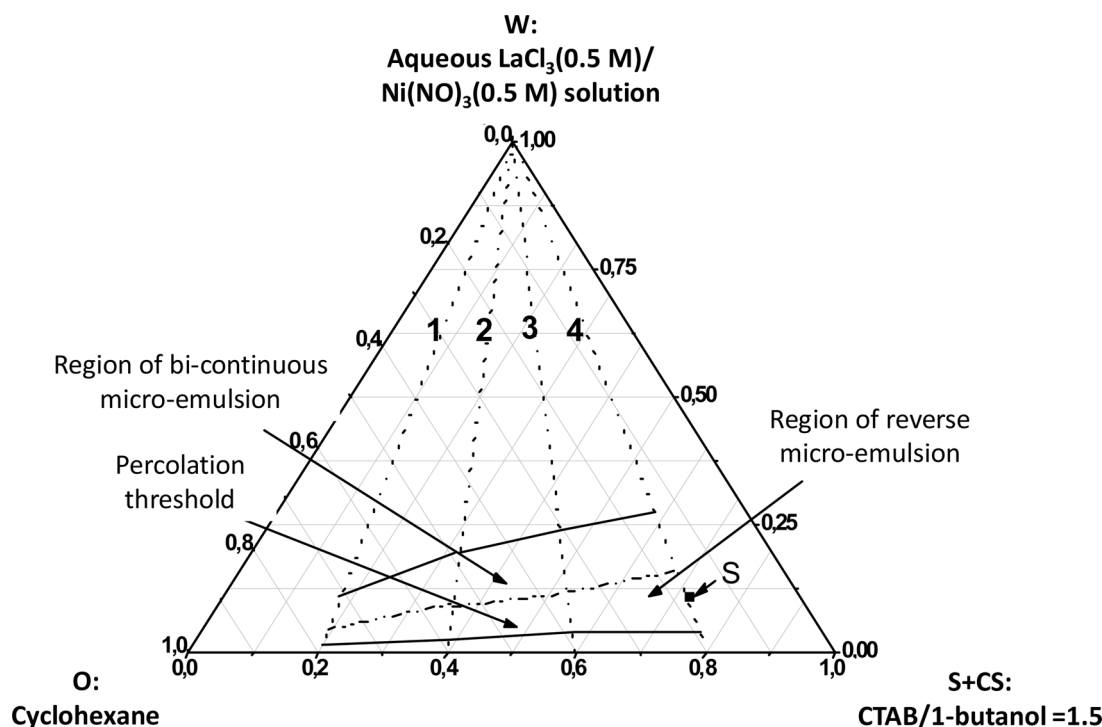


Fig. 1. Phase diagram of the reverse microemulsion system (the dashed dotted line roughly divided the region of the reverse micellar micro-emulsion from that of the bi-continuous micro-emulsion; S denotes the composition of the reverse micelle mixture from which perovskites were synthesized).

2. Experimental

2.1. Catalyst preparation

Single-reverse microemulsion technique was used to prepare the two nano sized perovskite (LaNiO_3 and LaCoO_3) catalysts using cetyltrimethylammonium bromide CTAB as surfactant (S), 1-butanol as co-surfactant (CS), and cyclohexane as oil phase (O) in adaptation of [29,30]. A pseudo ternary phase diagram was generated [29] (see Fig. 1) to find the best microemulsions compositions for preparation of two perovskite catalysts. Firstly, aqueous solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ containing a total metal concentration of 1 M (soln. W) was prepared. Solution W was added dropwise to different four solution, each of them containing the surfactant cetyltrimethylammonium bromide (S) and the co-surfactant 1-butanol (CS) in a mass ratio of 1.5:1 and different mass ratios of (S + CS) to oil, cyclohexane (O) (=0.2 (A1), 0.4 (A2), 0.6 (A3), and 0.8 (A4)), following the dashed lines 1–4 in Fig. 1. A variation in conductivity due to addition of solution W into S + CS + O is an indicator for the presence of the emulsion phases. The region of the reverse micelle micro-emulsion can be separated from the bi-continuous micro-emulsion by monitoring the change in the conductivity with increasing volume of solution W added [29]. The conductivity of the mixture was determined using a bench top Hanna conductivity meter at 25 °C using a circulating water bath.

Point S (which is the middle point in the reverse microemulsion region to ensure that emulsion formed will be reverse microemulsion) was chosen to prepare the perovskite samples. The metal cations were precipitated by the addition of an aqueous NH_3 solution (4 M) to the microemulsion S under vigorous stirring to obtain the corresponding perovskite. The resulting slurry was filtered, washed alternatively three times with a mixture of deionized water and alcohol, and dried at 100 °C overnight. The dried powder was grounded in an agate mortar and calcined at 750 °C for LaNiO_3 and 800 °C for LaCoO_3 for 4 h under atmospheric conditions.

2.2. Catalyst characterization

The crystal phases within the samples were determined using X-ray powder diffraction (XRD) carried out on Shimadzu XD-1 diffractometer in 2θ range between 20 and 80° with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$).

The morphology of the samples was characterized by high-resolution transmission electron microscopy (HR-TEM) spectroscopy. The TEM images were obtained on a JEOL 2100F operating at 200 kV. The prepared samples were suspended in ethanol for about 30 min under ultrasonic treatment then depositing on carbon-film-coated copper grids.

N_2 adsorption-desorption isotherms and pore size distribution were derived from the low temperature nitrogen (−196 °C) on a Quantachrome NOVA2000 gas sorption analyzer. The samples evacuated at 350 °C for 24 h prior to nitrogen adsorption.

The coke content of the spent catalysts was determined using thermal gravimetric analysis (TGA) carried out to using SETARAM Labsys TG-DSC16 model. The sample (ca. 10 mg) in air.

2.3. Catalytic activity

Steam reforming of glycerol was carried out in a continuous flow system consisting of a stainless steel fixed bed tubular reactor operating at atmospheric pressure using 0.2 g of the catalyst, which was diluted with 0.2 g of the same sized quartz particles. A water/glycerol mixture (36 wt.% glycerol) was fed into a preheater reactor at 150 °C by a dosing pump with a flow rate of 0.1 cm^3/min using nitrogen as carrier gas (40 $\text{cm}^3(\text{NTP})/\text{min}$). The reaction temperature was varied between 400 and 700 °C.

The product stream was analyzed using gas chromatography using with three columns. A molecular sieve 5A capillary column was used for the separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide and their subsequent detection using a TCD. Methane, carbon dioxide, ethane were separated on a Haysep P column and analyzed using a TCD. The third capillary column (DB-1) used for separation of methane, ethane, ethylene, acetaldehyde, ethanol, acetone with

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