Molybdenum carbide supported nickel–molybdenum alloys for synthesis gas production via partial oxidation of surrogate biodiesel

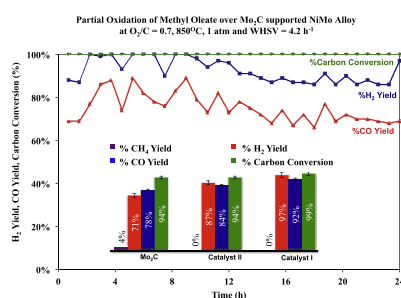Shreya Shah [a], Oscar G. Marin-Flores [b], M. Grant Norton [b], **, Su Ha [a], *

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HIGHLIGHTS

- Calcination temperature of 400 °C leads to high dispersion of NiMo alloys over Mo_2C.
- Mo_2C supported NiMo alloys show synergistic effect for POX of methyl oleate.
- The catalysts show the initial performance of 97% H_2 yield and 99% conversion.
- The catalysts show stable performance for 24 h on-stream.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

In this study, NiMo alloys supported on Mo_2C are synthesized by wet impregnation for partial oxidation of methyl oleate, a surrogate biodiesel, to produce syngas. When compared to single phase Mo_2C, the H_2 yield increases from 70% up to >95% at the carbon conversion of ~100% for NiMo alloy nanoparticles that are dispersed over the Mo_2C surface. Supported NiMo alloy samples are prepared at two different calcination temperatures in order to determine its effect on particle dispersion, crystalline phase and catalytic properties. The reforming test data indicate that catalyst prepared at lower calcination temperature shows better nanoparticle dispersion over the Mo_2C surface, which leads to higher initial performance when compared to catalysts synthesized at higher calcination temperature. Activity tests using the supported NiMo alloy on Mo_2C that are calcined at the lower temperature of 400 °C shows 100% carbon conversion with 90% H_2 yield without deactivation due to coking over 24 h time-on-stream.

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1. Introduction

With depletion of fossil fuels, the world is slowly moving towards a hydrogen economy [1,2]. One of the major applications of hydrogen is in fuel cells, wherein the chemical energy of the fuel is directly converted into electrical energy with water as the only by-product. This route for energy conversion allows the possibility of achieving higher fuel efficiencies compared to conventional heat engines [3]. Hydrogen-powered fuel cells find practical applications as part of auxiliary power units (APUs) for vehicles such as cars, trucks, ships and aircraft. However, on-board storage of large amounts of hydrogen to power fuel cells is not presently economically viable. Rather, it is more practical to produce hydrogen on demand via the reforming of liquid transportation fuels.

Currently, most hydrogen is produced by steam reforming of natural gas [4]. However, steam reforming is endothermic; requiring constant energy input for the generation of steam. Conversely, partial oxidation is exothermic with quick start up and fast response times [5]. It can also be performed in compact reactors, which can be useful for mobile fuel cell applications. As for the fuel, natural gas is not a renewable energy source and hydrogen generation from it does not help in addressing the environmental concerns due to a net production of carbon dioxide (CO_2) [6]. Biofuels, on the other hand, are renewable energy sources that allow the production of hydrogen with a net zero CO_2 emission: the CO_2 generated can be reutilized to produce additional biomass via photosynthesis [7,8]. Biodiesel is a biofuel that can be produced from various sources like animal fats or vegetable oils through trans-esterification [9]. Since it is produced from biomass, biodiesel does not impose a sulfur poisoning issue for catalytic materials. In the state of Washington, biodiesel is produced mainly from canola and contains almost no sulfur or aromatic compounds, being basically a mixture of methyl esters with methyl oleate as the major component [10]. Based on this compositional analysis, methyl oleate emerges as a suitable model compound for biodiesel.

There is a paucity of information in the literature regarding the reforming of biodiesel for hydrogen production. Recently, a study was conducted to investigate the production of olefins from biodiesel using $Rh-Ce-Al_2O_3$ catalysts produced at different temperatures and examining the influence of the oxygen to carbon molar ratios (O_2/C) on the product composition [11]. However, despite its high catalytic performance toward the reforming of biodiesel for hydrogen production, Rh-based catalysts are usually too expensive for commercial applications. On the other hand, Ni-based materials have been known as inexpensive catalysts for the reforming of hydrocarbons for hydrogen production [12,13]. However, Ni catalysts eventually deactivate due to coke formation [14,15], which makes clear the need to modify these materials in order to improve their coking resistance. Mo_2C is another inexpensive catalytic material that has been found to be active for the reforming of hydrocarbons due to its noble metal-like electronic structure. In addition, Mo_2C has shown the ability to reform long chain hydrocarbons with high resistance to deactivation due to coking [16,17]. Ni-modified Mo_2C catalysts have been previously used for methanol steam reforming [18], methane dry reforming [19], water-gas shift [20], electrocatalysis [21], and other processes where the presence of Ni enhances the catalytic performance of Mo_2C.

The calcination temperature at which a Ni-based catalyst is synthesized appears to be a key parameter since it can significantly alter the quality of the catalyst due to multiple factors. According to previous studies, the metal-support interactions become stronger as the calcination temperature increases [22–24]. Bartholomew et al. found that at high calcination temperatures NiO reacts with Al_2O_3 to form $NiAl_2O_4$ spinels, which are difficult to reduce even under severe reducing conditions [25]. Furthermore, high calcination temperatures are expected to increase the Ni particle size as a result of sintering, thus reducing the number of active reaction sites. Moreover, it has been reported that carbon formation on Ni particles is directly related to particle size and mostly starts over particles >7 nm [25]. Hence, it is important to use an optimum calcination temperature that leads to small Ni particles with a high dispersion over the Mo_2C surface. In addition, Ni and Mo are well known for forming alloys with enhanced resistance to corrosion [26] and with better catalytic activity towards reforming of hydrocarbons for syngas production [27].

The aim of the present study is to combine Ni and a coking-resistant catalyst such as Mo_2C to produce a catalytic material with high activity and stability for the partial oxidation of biodiesel. This work focuses on the effect that the preparation method (and particularly the calcination temperature) has on the structure and activity of the resulting catalyst for the partial oxidation of methyl oleate, which was selected as a model biodiesel compound.

2. Thermodynamic analysis

The partial oxidation of methyl oleate can be formulated as follows:

$$C_{19}H_{36}O_2 + 8.5\, O_2 = 19\, CO + 18\, H_2 \tag{1}$$
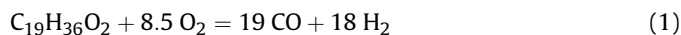
Along with partial oxidation, additional side reactions take place; however, for the sake of simplicity in our thermodynamic analysis it was assumed that such side reactions lead exclusively to the formation of C_1- and C_2-compounds (such as carbon dioxide, methane, ethane, ethylene and acetylene), in addition to H_2 and H_2O. Based on the minimization of Gibbs free energy approach, the effect of the O_2/C on the yields of H_2 and CO is shown in Fig. 1. Under the operating conditions used in this analysis (850 °C and 1 atm), the formation of CH_4 and C_2-compounds was found to be negligible. Fig. 1 also shows that O_2/C ratios ≥ 0.5 are required to prevent carbon formation, which is detrimental to the catalytic performance since it promotes deactivation. However, at O_2/C ratio ≥ 0.5 the reforming environment becomes more oxidizing, leading to a reduction in the production of syngas and an increase in the concentrations of H_2O and CO_2.

The reforming environment has been previously reported by our group to affect the stability of the metastable MoO_2 phase [28]. At O_2/C ratios ≤ 0.6 carburization of the oxide phase occurs leading to the formation of Mo_2C. On the basis of this information, the O_2/C selected in the present work was 0.6, which is expected to reduce coke formation and favor the phase transition of MoO_2 to Mo_2C without significantly decreasing H_2 yield.

The addition of Ni to a Mo oxide phase may lead to the formation of stable NiMo alloys. The Ni–Mo phase diagram indicates the possible formation of three alloys depending on the temperature and the amount of Ni present in the system: β-Ni_4Mo, γ-Ni_3Mo and δ-NiMo [29]. If the concentration of Ni is too high the resulting material may inherit the weaknesses of Ni-based catalysts, i.e., susceptibility to sintering and proneness to deactivation. On the other hand, too low concentrations of Ni may lead to negligible enhancements of Mo_2C in terms of both activity and stability.

3. Experimental

3.1. Catalyst synthesis

The materials used for catalyst synthesis were $Ni(NO_3)_2 \cdot 6H_2O$ as Ni precursor and MoO_2 as Mo_2C precursor, both obtained from
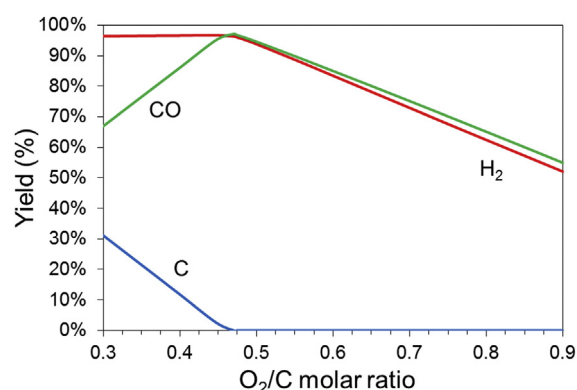
Fig. 1. Effect of O_2/C ratio on equilibrium compositions (1 atm, 850 °C).