INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 7735–7746

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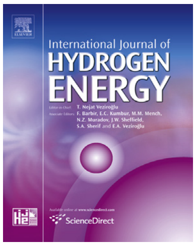

Steam reforming of ethanol over Ni-based catalysts: Effect of feed composition on catalyst stability

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ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form
9 March 2014
Accepted 16 March 2014
Available online 14 April 2014

Keywords:
Steam reforming
Ethanol
Nickel
Carbon deposition
Oxygen addition
Hydrogen addition

ABSTRACT

In this work the effects of steam-to-carbon ratio (S/C), and addition of H_2 or O_2 to the feed on the product yields and carbon deposition in the steam reforming (SR) of ethanol over Ni/$MgAl_2O_4$, Ni/$Ce_{0.6}Zr_{0.4}O_2$, and Ni/CeO_2 at 600 °C have been investigated. Increasing the S/C-ratio from 1.6 to 8.3 over Ni/$MgAl_2O_4$ increased conversion of ethanol as well as the yield of H_2, while the carbon deposition and yield of hydrocarbons decreased. Oxygen addition at S/C-ratio of 6 over Ni/$MgAl_2O_4$, Ni/$Ce_{0.6}Zr_{0.4}O_2$, and Ni/CeO_2 increased conversion, decreased the yield of hydrocarbons, and led to a decrease in the carbon deposition. Carbon deposition was almost eliminated over Ni/$MgAl_2O_4$ and Ni/$Ce_{0.6}Zr_{0.4}O_2$ at an O/C-ratio of roughly 0.8 or higher. The penalty of adding O_2 was a decrease in the yield of H_2 from 70% at $O/C = 0$ to 50% at $O/C = 0.8–1$.

A 90 h test at $O/C = 1.1$, $S/C = 6$, and 600 °C over Ni/$MgAl_2O_4$ showed stable behavior and an average rate of carbon deposition of less than 7 μg C/g_{Cat} h. The results indicate that stable operation of ethanol SR is only possible under oxidative conditions.

Introduction

Biomass is the only sustainable carbon source available and liquid fuels, like diesel and gasoline, might be produced from biomass in the future. However, biomass has a low energy density and is therefore expensive to transport over longer distances [1]. One possibility is to do a flash pyrolysis of the biomass, which, among other products, yields a liquid fraction called bio-oil or pyrolysis oil. The flash pyrolysis can be tuned to obtain a maximum yield of bio-oil around 75 wt% from wood and barley straw [2–5]. The advantage of converting biomass into bio-oil is lower transportation costs due to an up to ten times higher energy density of bio-oil compared with untreated biomass [1–4].

Abbreviations: HDO, hydrodeoxygenation; MAR, mass action ratio; SR, steam reforming; WGS, water gas shift; WHSV, weight hourly space velocity.

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http://dx.doi.org/10.1016/j.ijhydene.2014.03.107

Bio-oil contains mainly oxygenated compounds, which nevertheless induces a low heating value compared to fossil fuels as well as a low storage stability [6]. Polymerization of oxygenates in the bio-oil upon storage may increase the viscosity and lead to phase separation [6–8]. These issues make the bio-oil unsuited for direct utilization as a fuel and therefore upgrading of the bio-oil is needed. Thus, one concept for bio-oil utilization could be to conduct the flash pyrolysis of biomass close to the biomass production site and then transport the bio-oil to a (bio)refinery. Here upgrading of the oil through prospective catalytic processes like hydrodeoxygenation (HDO) or steam reforming (SR) can be performed [9–11]. HDO needs hydrogen to upgrade the bio-oil to transportation fuels, which can be produced through SR of bio-oil making the overall process sustainable [9,12–14]. One of the main challenges in SR of bio-oil is deactivation of catalysts due to carbon deposition on the catalysts [9,13–17], which will be addressed in this study.

In this study ethanol has been chosen as a model compound of bio-oil because it has an oxygen functionality which is found in bio-oil and similar to bio-oil is prone to carbon deposition on the catalysts leading to deactivation [18–20]. Furthermore SR of ethanol is in its own an interesting process as it can be used to provide for H_2 for fuel cells in mobile applications [21].

Steam reforming of ethanol can be described by the following reactions:

$$CH_3CH_2OH + H_2O \rightleftharpoons 2CO + 4H_2 \tag{1}$$

$$CH_3CH_2OH + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 \tag{2}$$

Reaction (1) is the general SR-reaction, while Reaction (2) assumes full shift of CO to CO_2 (Reaction (3)), which yields two additional moles of H_2. Beside the water-gas shift (WGS) reaction, the methanation reaction may also influence the product distribution:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{4}$$

The offgas composition is governed by the kinetics and equilibrium between the reactions shown above e.g. Reactions (1), (3), and (4). High temperatures will favor the reforming reaction and produce H_2 and CO as Reaction (1) is shifted toward the right, while Reaction (4) will be shifted to the left. The WGS, Reaction (3), will be shifted toward CO and H_2O at temperatures above 800 °C and therefore the maximum H_2 production is achieved at intermediate temperatures, 600–800 °C [22].

Side reactions observed in SR of ethanol are dehydration, Reaction (5), or dehydrogenation, Reaction (6), yielding ethene and acetaldehyde, respectively [21,23–28].

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \tag{5}$$

$$CH_3CH_2OH \rightarrow C_2H_4O + H_2 \tag{6}$$

Especially, formation of ethene is troublesome as it has a high potential for forming carbon deposits [26,29–31]. Carbon formation from ethene could occur through decomposition followed by accumulation and polymerization of carbon atoms [25,29,31]:

$$C_2H_4 \rightarrow 2C + 2H_2 \rightarrow \text{Carbon} \tag{7}$$

Alternatively, carbon deposits can be formed through direct polymerization of ethene [21,23,24]:

$$nC_2H_4 \rightarrow \text{Carbon} \tag{8}$$

Others routes to carbon deposition includes the Boudouard reaction (Reaction (9)), CO decomposition (Reaction (10)), and methane decomposition (Reaction (11)).

$$2CO \rightleftharpoons C_s + CO_2 \tag{9}$$

$$CO + H_2 \rightleftharpoons C_s + H_2O \tag{10}$$

$$CH_4 \rightleftharpoons C_s + 2H_2 \tag{11}$$

The carbon formed in Reactions (7)–(11), can be as carbon whiskers or gum depending on the temperature [32–34]. Carbon deposition is discussed further in the Supplementary Data.

Oxidative SR can be used to decrease carbon deposition as oxygen may react with carbon or carbon precursors on the surface of the catalysts. However, oxidative conditions will increase the formation of CO_2 and decrease H_2-production [13,35–44]. Among others, Cavallaro et al. [18] reported a decrease in carbon deposition from 0.28 mg/(g_{Cat} h) to 0.01 mg/(g_{Cat} h) at 650 °C and S/C-ratio of 4.2 over Rh/Al_2O_3 when adding O_2 to the feed gas at an O/C-ratio of 0.4. No carbon was deposited on a $La_{0.9}Ce_{0.1}NiO_3$-perovskite catalyst operated at 300–800 °C, S/C = 1.5, and O/C = 0.5 [41]. Furthermore it was shown that O/C-levels lower than 0.5 led to carbon deposition over $La_{0.9}Ce_{0.1}NiO_3$ at S/C = 1.5 and 500 °C [41]. The yield of H_2 depends on both S/C-ratio and O/C-ratio and Salge et al. [42] reported a maximum yield of H_2 in SR of ethanol under oxidative conditions of 57.5%, according to the definition of yield used in this work, at 600 °C, S/C = 4.5, and O/C = 0.66 over a Rh–Ce monolith catalyst. Peela and Kunzru [43] reported a drop in the yield of H_2 at 550 °C and S/C = 3 from 65% at O/C = 0 to 43% at O/C = 1.5. These results indicate that addition of oxygen to the feed may help solve the carbon deposition problem, but at the cost of a lower yield of H_2.

Another strategy to minimize the carbon deposition problem would be to add hydrogen to the feed. Hydrogen might hydrogenate unsaturated compounds like ethene and therefore decrease the deposition of carbon. Furthermore the additional H_2 will ensure that the catalyst is reduced under the reaction conditions. Laosiripojana et al. [44] investigated addition of H_2 at H/C-ratios between 0 and 5 at S/C-ratio of 1.5 and found a decrease in hydrocarbon yield and carbon deposition on Ni/CeO_2 and Ni/Al_2O_3 at 900 °C in SR of ethanol. The yield of CH_4 decreased from 10.6% at H/C = 0–7.1% at H/C = 5, while the carbon deposition decreased from 1.08 monolayers at H/C = 0–0.13 monolayers at H/C = 5 over Ni/CeO_2. Jacobs et al. [45] reported an increased conversion and methane formation with hydrogen addition over Pt/CeO_2 at 300 °C, S/C-ratio of 16.7, and H/C-ratios between 0 and 26.7 in the SR of acetic acid. The conversion increased from 5.4% at H/C = 0 to 35.6% at H/C = 26.7, while the yield of CH_4 increased