Steam Reforming of Glycerol

Subjects: Others
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In the last decades, environmental crises and increasing energy demand have motivated researchers to investigate the practical techniques for the production of clean fuels through renewable energy resources. It is essential to develop technologies to utilize glycerol as a byproduct derived from biodiesel. Glycerol is known as a sustainable and clean source of energy, which can be an alternative resource for the production of value-added chemicals and hydrogen. The hydrogen production via steam reforming (SR) of glycerol using Ni-based catalysts is one of the promising approaches for the entry of the hydrogen economy. The purpose of this review paper is to highlight the recent trends in hydrogen production over Ni-based catalysts using the SR of glycerol. The intrinsic ability of Ni to disperse easily over variable supports makes it a more viable active phase for the SR catalysts. The optimal reaction conditions have been indicated as 650–900 °C, 1 bar, and 15 wt% Ni in catalysts for high glycerol conversion. In this review paper, the effects of various supports, different promoters (K, Ca, Sr, Ce, La, Cr, Fe), and process conditions on the catalytic performance have been summarized and discussed to provide a better comparison for the future works. It was found that Ce, Mg, and La have a significant effect on catalytic performance as promoters. Moreover, SR of glycerol over hydrotalcite and perovskite-based catalysts have been reviewed as they suggest high catalytic performance in SR of glycerol with improved thermal stability and coke resistance. More specifically, the Ni/$LaNi_{0.9}Cu_{0.1}O_3$ synthesized using perovskite-type supports has shown high glycerol conversion and sufficient hydrogen selectivity at low temperatures. On the other hand, hydrotalcite-like catalysts have shown higher catalytic stability due to high thermal stability and low coke formation. It is vital to notice that the primary concern is developing a high-performance catalyst to utilize crude glycerol efficiently.

Keywords: hydrogen production ; steam reforming of glycerol ; Ni-based catalysts ; hydrotalcite ; perovskite

1. Introduction

In the last decades, environmental crises and increasing energy demand have motivated researchers to investigate the practical techniques for the production of clean fuels through renewable energy resources. It is essential to develop technologies to utilize glycerol as a byproduct derived from biodiesel. Glycerol is known as a sustainable and clean source of energy, which can be an alternative resource for the production of value-added chemicals and hydrogen. The hydrogen production via steam reforming (SR) of glycerol using Ni-based catalysts is one of the promising approaches for the entry of the hydrogen economy.

2. Steam Reforming of Glycerol

In recent years, the SR of glycerol as a process to utilize the crude glycerol obtained from biodiesel production plants has attracted many researchers. The main objective is to produce hydrogen from a renewable biomass resource and furthermore making biodiesel with more economical benefits [1][2]. The SR of glycerol Equation (1), includes glycerol decomposition Equation (2) and water–gas shift reaction Equation (3):

$$C_3H_8O_3\ (g) + 3H_2O\ (g) \leftrightarrow 3CO_2 + 7H_2\ (g) \qquad \Delta H_{25\ °C} = 128\ KJ/mol \tag{1}$$

The glycerol decomposition:

$$C_3H_8O_3 \leftrightarrow 3CO + 4H_2 \qquad \Delta H_{25\ °C} = 251\ KJ/mol \tag{2}$$

Water–gas shift reaction (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{25\,°C} = -41\ KJ/mol \tag{3}$$

The SR of glycerol may include a couple of secondary reactions, for instance, the methanation, Equations (4) and (5), methane dry reforming, Equation (6), and coke formation, Equations (7)–(10) [3][4]:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (\Delta H_{25\,°C} = -206\,kJ) \tag{4}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (\Delta H_{25\,°C} = -165\,kJ) \tag{5}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (\Delta H_{25\,°C} = 247\,kJ) \tag{6}$$

$$2CO \leftrightarrow CO_2 + C(s) \quad (\Delta H_{25\,°C} = -172\,kJ) \tag{7}$$

$$CH_4 \rightarrow 2H_2 + C(s) \quad (\Delta H_{25\,°C} = 75\,kJ) \tag{8}$$

$$CO + H_2 \rightarrow H_2O + C(s) \quad (\Delta H_{25\,°C} = -131\,kJ) \tag{9}$$

$$CO_2 + 2H_2 \rightarrow 2H_2O + C(s) \quad (\Delta H_{25\,°C} = 306\,kJ) \tag{10}$$

* Attapulgite.

It is crucial to notice that in the decomposition of glycerol, methane can be formed as an intermediate. Therefore, a high-performance catalyst which can perform both SR of methane and WGS reaction is needed to produce syngas and convert CO to CO_2, respectively [5].

Coke deposition leads to the catalyst deactivation and is considered as one of the main issues in the SR of glycerol. Therefore, many researchers have investigated developing a durable catalyst and enhanced reaction conditions. In this regard, it was found that the reaction conditions for SR of glycerol generally would be as follows: 700 °C, 1 bar, steam to carbon molar ratio of $H_2O/C_3H_8O_3$ = 9 to 12. It must be noted that the operation at such a high temperature would be tremendously difficult because the glycerol oxygen content is mildly high, and it causes lower thermal stability [6][7]. This fact implies the importance of implementing an efficient catalyst bearing the sintering and avoiding coke formation in the process. In other words, in the catalytic SR of glycerol, the development of a high-performance catalyst is an important factor for the commercialization of this process [8].

Many researchers have studied the effect of synthesis methods of the catalyst with modified supports (MgO, CeO_2, Al_2O_3, and TiO_2) and promoters (using various transition metals including Co, Cu, Zr, Ce, Rh, Ru, Pt and Pd, and Fe) to obtain high yields [9][10][11]. Ming et al. [12] reported that when using bare alumina as a catalyst, the hydrogen yield was 39%. However, when the catalyst was modified as Ni/Al_2O_3, Co/Al_2O_3, and La/Al_2O_3, these yields reached 47.7, 43.8, and 54.5%, respectively. The $Ni/La/Co/Al_2O_3$ catalyst showed the highest hydrogen yield, 77.7%. Kousi et al. [13] stated that the enhanced activity and high hydrogen yield in the SR of glycerol could be achieved by introducing La_2O_3 as a promoter to the Ni/Al_2O_3 catalyst. Table 1 listed a summary of process conditions for the SR of glycerol over Ni-based catalysts.

Table 1. Summary of process conditions for Ni-based glycerol steam reforming.

T (°C)	P (Bar)	$H_2O/C_3H_8O_3$ Molar Ratio	Support	Promoters	Ni Content wt%	Glycerol Conversion (%)	Ref.
500,650	1	3.7	La_2O_3-ZrO_2	-	15	99.9	[14]
400~800		3	CaO-ATP *	-	10	93.7	[15]
650	1	3.7	CeO_2–ZrO_2	La	12	99.9	[16]
550~650	-	9	Graphene	-	13~14.7	95.1	[17]
600	1	12	Al_2O_3/Al_2O_4	-	15	99.0	[18]
450~550	1	8~14	Fly ash	-	2.5,5,7.5,10	96.0	[19]
400~750	1	2.6	Al_2O_3,La_2O_3		8	70~92.0	[20]
500~650	1	3.7	TiO_2	La	15	99.7	[21]
650	-	3	ZrO_2	Pr,Ce,La,Yb	20	90	[22]
650	1	6~15	CeO_2,Al_2O_3,SiO_2	-	15	92	[23]
650	-	12	SiO_2	Mg	10	91~97.0	[24]
700	1	5	Zeolite Y/CeO_2	Cs or Na	13	99.0	[25]
400~700	-	9	ZrO_2	-	5	98.0	[26]
630	1	9	$NiAl_2O_4$	-	-	88.2	[27]
500	-	4	Al_2O_3, $AlCeO_3$	CaO	20	95.0	[28]

3. Perspective of Catalysts

Generally, the catalyst composition regarding the SR of glycerol typically consists of transition metals such as nickel (Ni) or noble metals such as platinum (Pt), ruthenium (Ru), and palladium (Pd), supported on alumina or perovskite-type catalysts that are doped with promoters to prevent the coke formation. The high costs of the noble metals shifted researchers to substitute them with the low-cost and available metals such as Ni [29]. Considering the SR of glycerol, C–C, C–H and O–H bond cleavages with conserving the C–O bonds are essentially important [30]. The hydrocarbon (C– C, O–

H, and C–H) bonds can easily break down in the presence of Ni, with the latter also capable of enhancing the water–gas shift reaction (WGS). Using supports such as aluminum oxide (Al_2O_3) can lead to improving the metal diffusion, obtaining appropriate acid–base sites, and consequently decreasing the coke deposition on the surface of the catalyst. Al_2O_3 is a metal oxide with proper thermal stability and specific surface area [31]. In recent decades, perovskite-type catalysts because of their special crystal structure are more attractive to researchers who focused on the hydrogen economy [1].

The catalytic application of hydrotalcite-like compounds and their derivatives have received extensive attention in the academic and industrial researches. Hydrotalcite-like (HTL) materials are double layered anionic clays with a 2D nanostructure considering the packed arrangement of OH groups where weak bonding between interlayer anions and structural sheets initiates the ion exchange feature and its physicochemical properties influenced by these anions. Its chemical formula is $Mg_6A_{l2}(OH)_{16}CO_34H_2O$, and the double hydroxides are layered. Hydrotalcites usually exist in nature with different forms, such as foliated, contorted plates or fibrous masses [2][32][33].

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