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Review article

Progress in the reforming of bio-oil derived carboxylic acids for hydrogen generation

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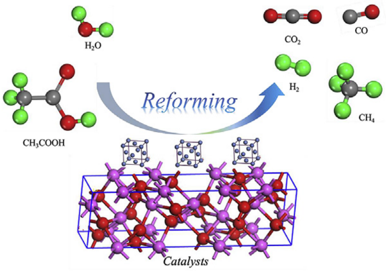
HIGHLIGHTS

- This study reviewed the progress of steam reforming of acetic acid.
- Various processes for acetic acid reforming were summarized and compared.
- The reactors used for steam reforming of acetic acid were discussed.
- Various catalysts developed for steam reforming of acetic acid were compared.
- The key challenges and the outlook for future research directions were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Carboxylic acids are major components of bio-oil. Investigation of reaction characteristics of carboxylic acids during steam reforming contributes to understanding of the reaction behaviors of bio-oil in reforming process. Acetic acid is a major carboxylic acid in bio-oil. The research activities on acetic acid steam reforming have been intensified in recent years. A number of reforming catalysts, reforming processes and reactors have been developed. The catalysts developed differentiate from each other in terms of activity, stability and resistivity towards coking, due to their distinct elemental compositions, structural configurations and surface properties. The reforming processes and the reactors used for steam reforming of acetic acid also varies substantially, imposing profound effects on the reforming of acetic acid. To assess state of the art of the catalysts/process/reactors develop for acetic acid steam reforming, a critical review is required to screen the intrinsic effects of these variables. This review focuses on the progress of steam reforming of acetic acid in three aspects: reforming processes, reactors and catalysts. The information from this review will be a useful reference for the research in steam reforming of bio-oil and other organics such as methanol, ethanol and acetone.

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1. Introduction

Hydrogen is one of the key feedstock in chemical industry. Traditionally, hydrogen is used in a large scale in ammonia synthesis, petroleum refinery and the synthesis of methanol and other fine chemicals [1]. Recently, hydrogen has gained special attention due to its application in fuel cell powered cars [2]. Hydrogen is a clean fuel. The only product from the use of hydrogen as fuel is water, which is thus an environmentally benign energy carrier. Production of hydrogen is always a very hot research topic [3,4]. In industry, the annual production of hydrogen worldwide is ca. 50 million tons [5]. The dominant routes for production of hydrogen is via steam reforming of natural gas (accounting for 48% hydrogen production) and petroleum oil (accounting for 30%), gasification of coal (accounting for 18%) or electrolysis of water [6]. Fossil fuels are obviously the dominant sources of hydrogen, but fossil fuels are not sustainable and their use associated with environmental emissions. Increasing attention has been paid on production of hydrogen from the renewable resources such as biomass in recent years [7–9].

Biomass is a sustainable source for production of hydrogen. Biomass can be gasified directly to a mixture containing mainly hydrogen, methane and carbon oxides. It could also be pyrolysed to produce a biocrude (bio-oil) and followed by the reforming of bio-oil to produce hydrogen [10]. Bio-oil has a much higher volumetric density than biomass and can be transported to a long distance at a much lower cost. However, bio-oil is a very complex mixture of organics [11,12]. Steam reforming of bio-oil involves a rather complex reaction network [13]. Without understanding the reaction behavior of the major components of bio-oil, it would be very difficult to understand the overall behaviors of bio-oil during steam reforming. Acetic acid is an important fraction of bio-oil [14,15]. Understanding the behaviours of acetic acid during steam reforming provides essential information for understanding behaviours of the carboxylic acids in bio-oil. In addition, acetic acid, like methanol, ethanol or other small organics, is a liquid fuel and can be reformed in-situ to provide hydrogen for the Proton Exchange Membrane Fuel Cell (PEMFC) powered vehicles.

The first work about investigation of the feasibility of steam reforming of acetic acid was performed by Wang et al. from National Renewable Energy Laboratory [16]. Following this pioneering work, Seshan et al. investigated the mechanism for steam reforming of acetic acid over Pt/ZrO_2 catalysts [17]. Hu et al. also started the study about steam reforming of acetic acid in 2004 and published their work in 2006 [18]. Since then, steam reforming of acetic acid has become a very hot research topic and an important branch in area of hydrogen production. More than 100 papers have been published. Various catalysts, reforming processes, and reactors have been developed [19–34]. The research works about steam reforming of methanol or ethanol have been frequently reviewed and summarized [35–37]. However, up to now, there is no review paper dedicatedly devoted to steam reforming of acetic acid. It is necessary to review and summarize the state of the art for steam reforming of acetic acid, in order to provide comprehensive information for the further development of this important research area.

In this review, the progress in the main aspects of steam reforming of acetic acid was analyzed and discussed. These include (1) the thermodynamic analysis of the decomposition, steam reforming and sorption enhance steam reforming of acetic acid; (2) the reaction mechanism of steam reforming of acetic acid; (3) the configuration/optimization of the reforming process; (4) the reactors for steam reforming of acetic acid; (5) the catalysts developed or tested for steam reforming of acetic acid.

2. Thermodynamic analysis

Thermodynamic analysis aims to understand the essential reaction parameters such as reaction temperature, steam to carbon ratio (S/C) and pressure on distribution of the products [38–41]. This helps to optimize operating conditions to maximize hydrogen production while minimize formation of the organic by-products and coke. Guilhaume et al. performed a thermodynamic analysis of the decomposition of acetic acid [39]. The distribution of the products was depicted in Figure S1 [39]. Acetic acid could be completely converted at 300 °C, but coke together with water was the main product. Steam reforming of acetic acid hardly took place, while the dehydration and polymerization of acetic acid dominated. The production of coke and water decreased with the increasing reaction temperature, and meanwhile the yields of CO and H_2 started to increase, indicating the occurrence of steam reforming reaction. Steam reforming of acetic acid dominated at high reaction temperatures, such as at 800 °C, where steam was consumed and coke was eliminated. CO and H_2 became the dominating products. Steam has a drastic effect on the product distribution from the decomposition or the reforming of acetic acid. The steam generated via decomposition of acetic acid or reverse water gas shift reaction is very limited. Adding external steam could substantially modify the reaction network.

Figure S2 shows the thermodynamic analysis of the effects of S/C and reaction temperature on distribution of the products during steam reforming of acetic acid [38]. With the increase of S/C, the production of H_2 and CO_2 were promoted, while the production of CH_4, CO and coke were suppressed. The increase of S/C increases the partial pressure of steam on catalyst surface, which favors the adsorption and activation of steam. This facilitates the reaction of steam with CH_4 via steam reforming, with CO via water gas shift reaction, with coke or coke precursors via gasification. All these reactions promote H_2 production. Steam, thus, played an essential role in enhancing hydrogen production. Reaction temperature also significantly affects steam reforming of acetic acid. At low reaction temperatures (i.e. < 300 °C), CH_4, CO_2 and coke were the main products, regardless of the S/C used. Steam reforming could not initiate to an appreciable extent. Therefore, the side reactions like decomposition of acetic acid dominated. With increasing reaction temperature, the steam reforming reactions accelerated and the hydrogen production reached a maximum at ca. 450 °C. The further increase of reaction temperature led to the decrease of hydrogen production, due to the initialization of the reverse water gas shift reaction, producing CO at the expense of H_2 and CO_2. Thus, the reaction conditions for acetic acid reforming have to be delicately regulated to maximize hydrogen production while to minimize the formation of the by-products and coke.

The thermodynamic analysis of aqueous phase reforming (APR) of acetic acid, sorption-enhanced steam reforming of acetic acid (SESR) and autothermal steam reforming of acetic acid were also conducted [38,40]. Basically, similar conclusions were reached, which were not detailed here but combined and discussed in other relevant sections. The thermodynamic analysis of the decomposition or steam reforming of acetic acid generally adopts a simplified approach that considers the formation of H_2, CO, CH_4 and CO_2 only from steam reforming of acetic acid. In acetic acid reforming, the reaction network is actually far more complex [42]. Not only the above gaseous products but also a number of complicated organic by-products like acetone and ketene are formed. The formation of these organic by-products significantly impacts the reaction network in acetic acid reforming. The trend for formation of the gaseous products like CO could also be different from that predicted from the thermodynamic analysis at certain circumstance. CO could be formed not only at the high reaction temperatures via water gas shift reaction, but also at the low reaction temperatures via decomposition of acetic acid [34]. The reaction network of acetic acid reforming is very complicated, understanding of which determines the development of efficient reactors and catalysts. Analysis of the reaction network of steam reforming of acetic acid was thus conducted in the next section.