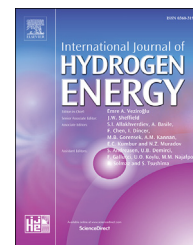




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Effect of W incorporation on the product distribution in steam reforming of bio-oil derived acetic acid over Ni based Zr-SBA-15 catalyst

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ABSTRACT

Zirconia incorporated SBA-15 type mesoporous material was synthesized following a one-pot hydrothermal route, characterized and used as the catalyst support in the synthesis of Ni and bi-metallic Ni–W based catalysts. Performances of these catalysts were tested in steam reforming of AcOH. Catalytic activity tests proved that the performances of SBA-15 and Zr-SBA-15 supported Ni based catalysts were highly stable and they also showed very high activity in steam reforming of acetic acid, giving complete conversion at temperatures over 700 °C. Product distributions were shown to be strongly influenced by the composition of the catalyst. In the case of 5Ni@Zr-SBA-15, syngas produced at 750 °C contained about 54% H₂, 22% CO, 20% CO₂ and 4% CH₄. These results indicated that decarboxylation reaction of AcOH to CH₄ and CO₂ was minimized over this catalyst. Results were considered to be highly promising for the production of hydrogen rich syngas. It was most interesting to observe that modification of this catalyst by the addition of tungsten caused significant changes in the product distribution. For instance, syngas produced over 5Ni-50W@Zr-SBA-15 at the same reaction conditions, contained equimolar quantities of H₂ and CO (about 47.5% each) with very small amounts of CO₂ and CH₄ (about 3% and 2%, respectively). Production of a syngas with such a composition was considered to be highly attractive from the point of view of a resource gas for dimethyl ether and Fischer-Tropsch synthesis.

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Introduction

Conventional production routes of hydrogen involve catalytic steam reforming of fossil resources, which generate large quantities of carbon gases. Fast depletion of fossil resources and environmental issues related to the extensive use of such resources as energy carriers has facilitated research activities for the production of hydrogen from renewable resources. Bio-

waste based bio-oil and bio-gas were recognized as promising resources for hydrogen production for mobile and stationary applications [1–6]. Recent developments in fuel cell technology have also accelerated the research studies for the production of hydrogen from bio-resources.

Acetic acid (AcOH) is a renewable, non-toxic and a safe bio-based hydrogen carrier. It is one of the main components of bio-oil, which can be produced by flash pyrolysis of biomass [3,7–11]. Flash pyrolysis of biomass may yield upto 80% bio-oil

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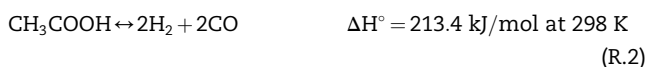
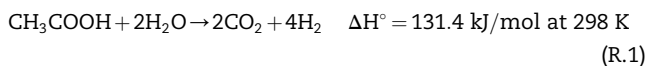
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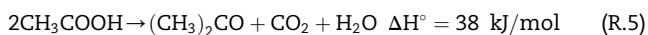
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and bio-oil may contain 12–19% acetic acid. Acetic acid may also be produced from biomass through fermentation. Hence, it is considered as an attractive renewable resource for the production of synthesis gas and/or hydrogen, through a catalytic steam reforming process [3,4,9–22]. As a result of steam reforming process of AcOH, a gas mixture which is mainly composed of H₂, CO, CH₄ and CO₂, is produced. Product distribution and the ratio of CO/CO₂ in the produced gas are expected to be strongly related to the catalyst composition and reaction conditions. This gas mixture can be used as a fuel in solid oxide fuel cells or to obtain high purity hydrogen for chemical applications [23,24]. Syngas thus produced can also be used as a resource for the production of valuable chemicals and fuels through Fischer-Tropsch or dimethyl ether synthesis routes. In such cases, a gas composition with equimolar quantities of H₂ and CO is generally preferred.

Steam reforming of AcOH, is an endothermic reaction, which is favored at high temperatures. Overall stoichiometry of steam reforming of AcOH reaction indicates the possibility of production of 4 mol of H₂ from 1 mol of AcOH (R.1). Production of hydrogen from acetic acid mainly involves thermal decomposition (R.2) and water gas shift reaction (R.3). However, steam reforming of acetic acid is a complex process with number of side reactions which affect the product distribution. Formation of methane and acetone, as well as thermodynamic limitations of water gas shift reaction decrease the hydrogen yield from the maximum possible value of 4 mol per mole of acetic acid reacted. Thermodynamics of water shift reactions are favored at low temperatures. Hence, this reaction will shift toward CO and H₂O at temperatures above 800 °C [25].



Occurrence of decarboxylation reaction (R.4) would cause formation of methane. Formation of some acetone was also reported in the literature (R.5). Coke formation is an important problem faced during steam reforming of AcOH since it causes catalyst deactivation, as well as clogging of the reactor. Coke formation over the catalyst may take place through Boudouard (R.6) and cracking (R.7) reactions.



Synthesis of active, stable and selective catalysts, which will give high hydrogen yields and will minimize coke

formation during steam reforming of acetic acid, is a challenging research area. Product distributions are also expected to be strongly dependent on the catalyst composition. Results reported in the recent literature showed that Pt, Pd, Rh, Ru and Ni based catalysts gave high activity in steam reforming of AcOH [9,12,17–20,26–31]. High activity of Ni based catalysts is considered to be mainly due to their ability to break the C–C, C–H and O–H bonds. Due to its low cost and high activity, Ni based catalysts attracted major attention of researchers in steam reforming reactions. However, significant amount of coke formation was reported in steam reforming of AcOH over Ni based catalysts. Particularly in recent years, efforts have been made to prevent carbon formation by working with monometallic Ni based catalysts [32–37] as well as bimetallic Ni-metal based catalysts [38–41].

Type of support material is expected to have strong influence on the performance of Ni based catalysts in steam reforming of AcOH. Invention of silicate structured mesoporous materials, like MCM-41 and SBA-15, opened new avenues in catalysis research. These materials, with ordered pore structures, were reported to be less susceptible to deactivation due to coke formation than the conventional microporous catalyst supports. They also cause less resistance to diffusion of reactants to the active sites [42–46]. However, some of the silicate structured mesoporous materials were known to have low hydrothermal stability in the presence of water vapor. Zirconia, with its high thermal and chemical stability attracted the attention of catalysis researchers in recent decades [43,46–49]. Strong interaction of Ni clusters with zirconia and quite high water dissociation capacity of zirconia were reported as attractive properties of this material in steam reforming reactions. More recently, zirconia incorporated SBA-15 was reported as a highly stable catalyst support for steam reforming of ethanol [47–49], glycerol [50], propylene glycol [51], methane [52] and dry reforming of methane reactions [53–55].

In a previous study of ours, it was shown that modification of mesoporous alumina supported Ni catalysts with W caused significant improvement in catalyst stability, which was mainly due to coke minimization during dry reforming of methane [56,57]. Redox ability of tungsten oxide helped coke minimization. In the present study, zirconia incorporated SBA-15 type mesoporous materials with different Zr/Si ratios were synthesized following a one-pot hydrothermal route. Performances of Zr-SBA-15 supported Ni and bi-metallic Ni–W catalysts were investigated in steam reforming of AcOH. Effects of zirconia incorporation into SBA-15 and W addition to Ni based catalysts on product distribution and coke formation were investigated and valuable information was obtained for the effect of catalyst composition on the product distribution.

Experimental

Synthesis and characterization of SBA-15 and Zr-SBA-15 supported catalytic materials

Silicate structured mesoporous SBA-15 was synthesized following a hydrothermal procedure [45,58]. In this procedure, triblock copolymer Pluronic® P123 (Sigma-Aldrich) was used

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