



Steam reforming of acetic acid over Ni/ZrO₂ catalysts: Effects of nickel loading and particle size on product distribution and coke formation

Zhikun Li^{a,b}, Xun Hu^{a,b}, Lijun Zhang^c, Shaomin Liu^c, Gongxuan Lu^{a,*}

^a National Engineering Research Center for Fine Petrochemical Intermediates, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

^b Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

^c Department of Chemical Engineering, Curtin University, Perth, WA6845, Australia

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ABSTRACT

Steam reforming of acetic acid has been carried out over a series of Ni/ZrO₂ catalysts to measure the effects of nickel loading on distribution of the reforming products and coke formation. Ni (≤ 13 wt.%) / ZrO₂ catalysts do not contain enough active metal sites for steam reforming of both acetic acid and organic by-products. Ni (≥ 20 wt.%) / ZrO₂ catalysts can effectively catalyze steam reforming but lack selectivity, since methanation and reverse water gas shift reactions are promoted, leading to low hydrogen yields. Ni (16 wt.%) / ZrO₂ catalyst is the most selective one, due to its low activity to the secondary reactions that contribute to by-product production. Coke formation is suppressed with the increase of nickel loading up to 16 wt.%, and then restarts to increase with the further increase of nickel loading. Polymerization of acetone is the main route for coke deposition over the Ni (≤ 13 wt.%) / ZrO₂ catalysts. Methane decomposition and CO disproportion are the two main routes for coke formation over the Ni (≥ 20 wt.%) / ZrO₂ catalysts, and methane contributes more to coke formation than CO. In addition, activity of Ni/ZrO₂ catalyst towards the secondary reactions such as methanation, reverse water gas shift reaction, methane decomposition, and CO disproportion are closely related to nickel loading and nickel particle sizes.

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1. Introduction

Bio-oil is a renewable resource derived from biomass, which is environmental benign and has been regarded as a potential source for bio-hydrogen production [1–7]. However, bio-oil is a complex mixture of organic compounds [8,9] and its steam reforming is characterized with lots of difficulties [10]. Steam reforming of the model components in bio-oil is relatively easier, and it can provide information about optimization of reaction parameters for steam reforming of the real bio-oil and preparation of active reforming catalysts. Acetic acid is one of the main acids in bio-oil [11] and a safe hydrogen carrier due to its non-flammable nature. Thus, steam reforming of acetic acid has been widely performed by different research groups [12–30].

The catalysts employed in the works concentrated on Ni-based catalysts and noble metal catalysts. The Ni-based catalysts are more promising in industrial application, due to their much lower cost. However, Ni-based catalyst is not selective and subjected to coking, which lowers the efficiency of steam reforming. Catalytic selectivity and stability of Ni catalyst are affected by many factors such

as nickel loading, promoters, supports, catalyst preparation procedure, and experimental conditions. In this study, the effects of nickel loading on catalytic behaviors of Ni catalysts are focused on, since the nickel loading significantly affects the dispersion of nickel species on support. The effects of nickel loading on the steam reforming of methane and ethanol have been performed by some researchers [31–33]. The nickel loading played a key role to determine the reaction network during steam reforming, which further affected the hydrogen production and the coke formation. Generally, an optimum of nickel loading exists over the different carriers, at which the production of hydrogen was maximized while coke formation was minimized. The nickel loading on the support affected the interaction of nickel with the support and the nickel dispersion on the support (Ni particle sizes), which further affected the catalytic behaviors during steam reforming.

In general, the metal species tends to be highly dispersed across carrier at low metal loadings, while the metal particles tend to aggregate at high metal loadings, forming large particles in size. What is the relation between the dispersion state of Ni particles and their catalytic behaviors? Understanding of this relation can help us to understand the dispersion–activity relations and prepare active, selective, and stable Ni catalyst. ZrO₂ contains acidic/basic features, which can enhance the adsorption of steam and carbon oxides onto its surface, resulting in an enhancement in hydrogen

* Corresponding author. Tel.: +86 931 4968178; fax: +86 931 4968178.

E-mail address: gclu@lzb.ac.cn (G. Lu).