



Pruning of the surface species on Ni/Al₂O₃ catalyst to selective production of hydrogen via acetone and acetic acid steam reforming

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ABSTRACT

Catalytic behaviors of the different metallic Ni species on Ni/Al₂O₃ catalyst surface were investigated in steam reforming of acetone and acetic acid to hydrogen. The different Ni species showed distinct activities for activation of acetic acid and acetone, gasification of coke precursors, and other secondary reactions such as methanation, water–gas shift reaction, CO disproportionation and methane decomposition. The Ni species weakly interacted with alumina solely showed negligible reforming activity, while the Ni species mildly interacted with alumina was very active and efficient for steam reforming reaction. In comparison, the Ni species strongly interacted with alumina existed in bigger particle sizes, which resulted in the side reactions for by-product generation and consequently led to serious coking. Suppression of its presence on catalyst is the key point to obtain a highly selective and stable Ni/Al₂O₃ catalyst.

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1. Introduction

Hydrogen is a clean fuel with a potential application in fuel cells [1–3]. Although hydrogen has been traditionally produced from nature gas or coal for decades [4–8], its production from renewable resource such as bio-oil has attracted more interest recently, which is due to the carbon-neutral and renewable natures of bio-oil [9,10]. Nevertheless, bio-oil is a very complex organic mixture and ranged from the light compounds such as ketones, carboxylic acids to the heavy compounds such as sugars [11–13]. The direct steam reforming of bio-oil always generates by-products and unacceptable levels of coke, leading to rapid deactivation of catalysts [14,15]. Developing selective and coke-resistant reforming catalyst is a key challenge for successful application of bio-oil as a resource of hydrogen. Optimizing catalyst components and modifying the catalysts with various additives have been confirmed as potential methods to develop active and stable catalyst for steam reforming of the bio-oil derived compounds, such as ethanol and acetic acid [16–32]. However, few attempt has been devoted to prune surface species of a reforming catalyst for deep understanding the dependence of the catalytic behaviors on the surface species, to obtain highly selective and stable heterogeneous catalyst for the steam reforming of bio-oil.

Ni/Al₂O₃ is widely used catalyst for steam reforming of organics to hydrogen [33,34]. However, Ni/Al₂O₃ catalyst is subject to coking, which leads to its fast deactivation during steam reforming [35,36]. The coke formation related to not only the properties of the reactants but also the state of the nickel species on alumina. It is known that nickel oxide (NiO) is inert for steam reforming [37–41] while the metallic nickel (Ni) is active. Therefore, the catalytic performance of Ni/Al₂O₃ catalyst is mainly determined by the characteristics of metallic Ni species on alumina. During the preparation and pre-treatment of Ni/Al₂O₃ catalyst, Ni species on catalyst surface may form many states and may interact with support via different ways. In this paper, three kinds of nickel species were identified, characterized, and tested for steam reforming of bio-oil model compounds. Their catalytic activities for steam reforming of acetone and acetic acid were investigated, respectively. Moreover, the catalytic activities of the different nickel species for the secondary reactions involved in steam reforming were also investigated. As a consequence, the dependences of catalyst activities on the states of Ni species were elucidated.

2. Experimental

2.1. Catalyst preparation

Ni/Al₂O₃ catalyst were prepared by incipient wetness impregnation method using Ni(NO₃)₂·6H₂O as a precursor. The metal loading to alumina was 25 wt.%. Before impregnation, the support

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