



Full Length Article

Steam reforming of acetic acid over Ni/Al₂O₃ catalysts: Correlation of nickel loading with properties and catalytic behaviors of the catalysts

Zhanming Zhang^a, Xun Hu^{a,*}, Jiaojiao Li^a, Guanggang Gao^a, Dehua Dong^a, Roel Westerhof^b, Song Hu^c, Jun Xiang^c, Yi Wang^{c,*}

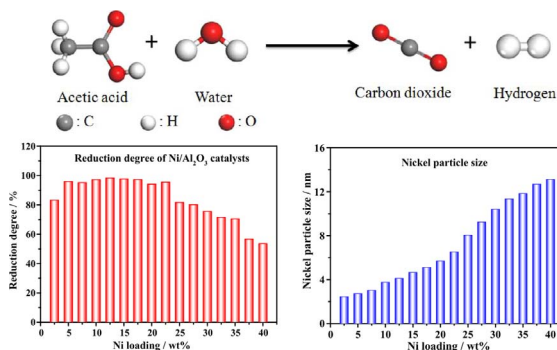
^a School of Material Science and Engineering, University of Jinan, Jinan 250022, PR China

^b SuSTER BV Mooienhof 203, EE Enschede, 7512, Netherlands

^c School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China



GRAPHICAL ABSTRACT



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ABSTRACT

In this study, steam reforming of acetic acid over the Ni/γ-Al₂O₃ catalysts with varied nickel contents (from 2.5 to 40 wt%) was performed, aiming to investigate the effects of nickel loading on properties and catalytic behaviors of the catalysts. The results show that the interaction of nickel species with alumina varies with varied nickel loading. At lower nickel loadings, the nickel strongly interacting with alumina are the main species, while with the saturation of the reactive sites of alumina via loading more nickel, the proportion of the nickel species weakly interacting with alumina increased remarkably. Excess nickel on alumina can fill the pores, decreasing the reduction degree of nickel oxides, the specific area (from ca. 277 to 132 m² g⁻¹ with the increase of nickel loading to 40 wt%), the pore volume, and the pore diameters. Nickel loading also significantly affects the catalytic activity, stability of the catalyst and the resistivity towards coking. With the increase of nickel loading to 10 wt%, the activity of the catalyst reached a plateau. The further increase of nickel loading did not further increase the activity, but increased the stability and the tolerance towards the deactivation induced by coking. In addition, with higher nickel loadings, the coke formed has more large aromatic ring system.

1. Introduction

Hydrogen is a clean source of energy, which has important

applications in chemical/petroleum industry and in fuel cells. The industrial routes to generate hydrogen are steam reforming of natural gas or naphtha or gasification of coal [1–3]. However, these traditional

* Corresponding authors.

E-mail addresses: mse_hux@ujn.edu.cn (X. Hu), alenwang@hust.edu.cn (Y. Wang).

feedstock for hydrogen production are not renewable and their use are associated with environmental emissions. Biomass is an alternative feedstock for hydrogen production, which is sustainable, renewable, carbon-neutral and has much lower emission of NO_x and SO₂ during the use.

Biomass can be directly gasified to syngas [4], or be pyrolysed to a condensable crude, named as bio-oil. Bio-oil can be steam reformed, as that of methanol and ethanol, to hydrogen. Bio-oil is a mixture of hundreds of components, while carboxylic acids such as acetic acid are the main component with the abundance of 5–10 wt% [5]. The concentration of acetic acid in the aqueous phase of bio-oil is even higher [6]. Steam reforming of acetic acid can provide useful information for understanding the reaction network of bio-oil, especially the carboxylic acids in bio-oil. Thus, acetic acid reforming has attracted great attention [7–25].

Many catalysts such as Ni-based catalysts [26–32], Co-based catalysts [33–38], Fe-based catalysts [39–41] and the noble metal catalysts [42–45] have been evaluated in steam reforming of acetic acid. Among them, the Ni-based catalysts have been investigated intensively [46–54]. Coking is one of the most challenging issues for the nickel-based catalysts, which relates to not only the properties of nickel species on the catalyst but also the property of the carrier supporting nickel.

In most cases, a support is used to increase the dispersion and thermal stability of the active species like nickel. However, support is generally not an inert material, which interacts with nickel and even modified the properties and catalytic behaviors of nickel species. The interaction of nickel with support is a very important parameter to be considered during evaluation of the catalyst, as it has substantial influence on the catalytic performance. Our previous study have confirmed that there are different type of nickel species on alumina with weak, mild to strong interaction with the support [54,55]. The interaction in essence is a solid phase reaction between nickel and the “reactive sites” of alumina, as evidenced by the formation of NiAl₂O₄ at high calcinations temperature [56,26]. It is believed that the “reactive sites” on alumina is limited, and not all nickel would react with alumina to the same degree. In another word, the “reactive sites” on alumina can be saturated and nickel loading would significantly affect the interaction of nickel species and alumina.

To confirm this, seventeen Ni/ γ -Al₂O₃ catalysts with the nickel loading varied from 2.5 to 40 wt% with a 2.5 wt% increment were prepared, characterized and evaluated in steam reforming of acetic acid. The effects of nickel loading on the reduction behaviors of nickel oxides, nickel particle size, specific area and pore distribution of the support, catalytic activity, stability, resistivity to coking and properties of coke were investigated in detail. The results confirmed the significant influence of nickel loading on the above parameters, which also serves as a reference to prepare the nickel-based catalyst with the desired nickel loading and desirable catalytic performance.

2. Experimental section

2.1. Catalysts preparation

The Ni/ γ -Al₂O₃ catalyst with different nickel loading was prepared by an equivalent wetness impregnation method using nickel nitrate as the metal precursor. Before impregnation, commercial γ -Al₂O₃ with a diameter between 45 and 60 mesh was washed several times with distilled water and then pretreated in an oven at 105 °C for 6 h until completely dried and then calcined at 600 °C for 4 h. Definite amount of Ni(NO₃)₂·6H₂O, which was calculated according to the specific nickel loading on alumina, were dissolved in distilled water with the aid of ultrasound. The aqueous solution of nickel nitrate was then added into the γ -Al₂O₃ carrier under constant stirring at room temperature. After that, the sample was aged at room temperature for 24 h and was then transferred to an oven and dried for 5 h at 105 °C. Finally, the samples

were calcined in a muffle furnace at 600 °C for 4 h.

2.2. Characterization of the catalysts

Hydrogen-temperature programmed reduction (H₂-TPR) was conducted in a U tube quartz reactor to evaluate the reduction behavior of the calcined catalysts by using a Vodo VDSorb-91x instrument. A powered sample (ca. 20 mg but precisely weighted) was pretreated at 105 °C for 1 h to remove physically absorbed water from the catalyst. Upon cooling to 50 °C, a flow rate of 20 mL/min of 5 vol% H₂/Ar was used for the reduction of the catalyst at the temperature from 50 to 950 °C at a ramping rate of 10 °C/min. The consumption of hydrogen was monitored by a thermal conductivity detector (TCD).

X-ray diffraction (XRD) patterns were performed with a X-ray diffractometer (XRD, Bruker D8-Advance, Cu K α target, λ = 1.5406 Å) with 2θ values between 10 and 90°. The catalysts were reduced by a gas mixture (hydrogen: nitrogen = 60 mL/min: 60 mL/min) at 600 °C for 1 h with a heating rate of 20 °C/min before conducting the XRD test.

Temperature programmed oxidation (TPO) was conducted in a U quartz tube to evaluate the coke species by using PCA-1200 instrument. Prior to the TPO test, a sample was dried at 100 °C under high-purity Ar to remove absorbed water for 1 h. After that, 50 mg catalyst loaded was heated to 800 °C at a ramping rate of 20 °C/min in a 5% O₂/He flow (10 mL/min).

TPO-MS were also conducted by measuring the change of the abundance of CO₂, CO and O₂ using an in-situ mass spectrometer (Pfeiffer, MS GSD 320). Mass spectrometry (MS) is a qualitative and quantitative method for the determination of the ion-mass ratio of samples. The mass spectrometer is calibrated with the standard gas (including N₂, H₂, CH₄, CO, CO₂) prior to testing. The outlet of the gases from the TPO tests was connected with the MS. The ions of 44 (CO₂), 28 (CO) and 32 (O₂) were selected for the measurement.

The specific area of the different catalysts was determined by N₂ adsorption-desorption measurement at 77 K by employing the Brunauer-Emmett-Teller (BET) method with the instrument of SSA-6000. Prior to the N₂ adsorption, the sample was degassed at 200 °C overnight to remove the moisture adsorbed on/in the porous structure.

TG/DTA (TG8121 Rigaku Corp.) was used to investigate the amount of carbon formed over the catalysts after the catalytic tests. The sample was heated from room temperature to 900 °C at a ramping rate of 20 °C/min in air (50 mL/min) and the weight change was recorded.

Elemental analysis (EA) was conducted to analyse the coke species formed on the catalysts by using a EuroEA3000-Single instrument. The contents of C, N, H and S elements were measured by high temperature combustion. After the samples were burned at 1150 °C in the combustion tube, the carrier gas of He was blown into different adsorption tubes for adsorption, and the element contents were detected by TCD detectors.

EDS-Mapping was conducted to analyze the distribution of Ni, Al and O elements by using FESEM, FEI, QUANTA FEG 250. A small amount of the sample was dispersed in an ethanol solvent and sonicated into a uniformly mixed solution. The distribution of Ni, Al, O elements in the microstructure of the material were analyzed by an energy dispersive spectrometer (EDS).

Raman was conducted to analyze the aromatic ring structure of the coke formed by using Horiba LabRam HR Evolution instrument. Raman spectroscopy is based on the Raman scattering effect and the incident light frequency of the different scattering spectrum analysis to get the molecular vibration and rotation information.

Transmission electron microscope (TEM) was conducted to observe the fine structure of the catalyst by using JEOL2010 instrument. About 5 mg catalysts was dispersed in an ethanol solvent and sonicated into a mixture. Subsequently, a copper grid was putted in the specimen holder and then put the dispersed mixture on the copper grid.

High performance liquid chromatography (HPLC) was conducted to analyse the concentration of acetic acid and acetone in the liquid

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