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Short Communication

Steam reforming of bio-oil derived small organics over the Ni/Al_2O_3 catalyst prepared by an impregnation–reduction method

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ABSTRACT

An impregnation–reduction method has been developed in this study to prepare the Ni/Al_2O_3 catalyst for steam reforming of bio-oil model compounds for hydrogen production. This method can alleviate the interactions between nickel species and an alumina carrier and promote metal dispersion and utilization of the nickel species, achieving a highly active, selective and stable reforming catalyst. Moreover, this method is very simple and fast. Only the impregnation and reduction steps are involved and the catalyst can be prepared in situ. In addition, coke formation in steam reforming is not uniform on a catalyst bed. Coking in the topmost catalyst layer is much more serious.

1. Introduction

Hydrogen, a clean energy carrier, has potential applications in fuel cell systems. Production of hydrogen from a renewable resource such as bio-oil, the condensable liquid crude from the pyrolysis of biomass, has attracted great attention due to the carbon-neutral feature of bio-oil [1–11]. However, bio-oil is a complex mixture of organics [12] and its steam reforming is characterized with lots of difficulties [13]. Developing a highly efficient reforming catalyst is crucial for the application of bio-oil as hydrogen feedstock.

Ni-based catalysts such as Ni/Al_2O_3 are widely applied in steam reforming reactions [14–22], due to its low cost. The nickel species is active for steam reforming, and its catalytic behaviors can be drastically modified when supported on a carrier such as alumina, due to the potential interaction between them. The interaction can be beneficial, since it can help to anchor the nickel species, preventing the fast sintering of nickel under thermal conditions. Nevertheless, the interaction may also be undesirable, since the interaction, especially a strong interaction, leads to a difficulty in the reduction of the nickel species. This will lower the utilization efficiency of the surface nickel species and may also lead to poor catalytic performances and the coking problem.

Controlling the extent of interaction between a nickel species and alumina support is important to obtain a highly efficient Ni/Al_2O_3 catalyst. Impregnation is a traditional method for preparing the Ni/Al_2O_3 catalyst, which involves an impregnation, drying, calcination, and reduction process. The nickel species in the catalyst prepared by this method can be hard to reduce, due to its strong interaction with an alumina carrier, reducing the utilization efficiency of the nickel species. In this study, a strategy using impregnation–reduction to prepare the Ni/Al_2O_3 catalyst has been developed. The method is very simple and fast. Only impregnation and reduction steps are involved and the catalyst is prepared completely in situ. The catalyst prepared by this method is proven to be very active, selective and stable by steam reforming of the mixture of acetic acid, ethanol and acetaldehyde.

2. Experimental

The catalyst was prepared by an impregnation–reduction method, which is detailed as follows. The quartz reactor (inner diameter: 6 mm, length: 50 cm) is filled up with the support γ-Al_2O_3 (pellets, diameters: 0.55–0.83 mm; pretreated in air at 650 °C for 6 h before use, total weight: 42 g) and the temperature is increased to 80 °C with nitrogen as the carrier gas (flow rate: 20 ml/min). Then, a saturated solution of $Ni(NO_3)_2$ (3.3 mol/l) is introduced into the reactor by a syringe pump with a flow rate of 0.26 ml/min for 1 h. After impregnation, the catalyst precursor is directly reduced with pure hydrogen at 600 °C for 3 h and then cooled to a given temperature in an inert nitrogen flow (20 ml/min)

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for steam reforming. Nickel loading calculated is 16 wt.% to Al_2O_3, which was determined by ICP-AES by digestion of the nickel oxides on catalyst support with concentrated nitric acid. The procedures for the Ni/Al_2O_3 catalyst prepared by the traditional wet impregnation method are as follows. $Ni(NO_3)_2 \cdot 6H_2O$ is used as the metal precursor and the metal loading is 16 wt.% to Al_2O_3. The wet impregnation is performed at room temperature by adding the $Ni(NO_3)_2$ solution which can be just adsorbed by the support used. After impregnation, the catalyst precursor is dried at room temperature for 24 h and at 110 °C for another 24 h. Finally, the precursor is calcined at 600 °C for 4 h and reduced in hydrogen at 600 °C for 3 h.

Catalytic tests are carried out in a fixed bed continuous flow quartz reactor at atmospheric pressure. A mixed solution of acetic acid, ethanol, and acetaldehyde (molar ratio: 1:1:1) is prepared to simulate the light components in bio-oil. It should be clarified that the simulated bio-oil here is different from the bio-oil produced from the pyrolyzed biomass. The pyrolyzed bio-oil contains a number of light and heavy organic compounds, including the sugar derived light components (i. e. carboxylic acids, aldehydes, ketones and alcohols), sugars (i. e. glucose, levoglucosan, and xylose), and phenolics (i. e. phenol and other big aromatics) [23–28].

The reactants (simulated bio-oil) are fed into a pre-heater (80 °C) by a syringe pump with a given liquid hourly space velocity (LHSV) and steam to carbon ratio (S/C) with nitrogen as the carrier gas (40 ml/min). Quantification of the products is achieved by two on-line chromatographs equipped with 5A and 13× molecular sieves as the columns. Overall conversion of the mixed organics ($X_{organics}$) is calculated by dividing the amount (mol basis) consumed with the amount loaded (mol basis). Product composition is calculated based on molar fraction of the products.

Hydrogen temperature-programmed desorption (H_2-TPD) measurements were performed using Ar as a carrier gas (40 ml/min). Before measurements, catalyst samples (150 mg) were reduced at the specific temperature to form the catalyst with the given nickel species, cooled in flowing H_2 to room temperature, and purged by the carrier stream until baseline stabilized. The desorbed H_2 was monitored and quantified by a TCD. To calculate metal dispersion, an adsorption stoichiometry of $H/Ni = 1$ (mol basis) was assumed. X-ray diffraction spectra (XRD) measurement is performed on a Philips X'pert MPD instrument using Cu K α radiation in the scanning angle range of 15–90° at a scanning rate of 4°/min at 40 mA and 50 kV. Coke on catalyst surface is analyzed by thermo-gravimetric analysis in a PerkinElmer TG/DTA apparatus. The catalyst is heated at 10 °C/min under oxidative atmosphere (oxygen content: 5 wt.%) and the mass loss is recorded (experimental error: ±0.5%).

3. Results and discussion

3.1. Characterizations of the prepared catalysts

XRD characterization is performed over the reduced Ni/Al_2O_3 catalyst prepared by the traditional impregnation method (TIM catalyst) and the reduced Ni/Al_2O_3 catalyst prepared by the impregnation–reduction method (IRM catalyst). Diffraction patterns are presented in Fig. 1. The diffraction pattern of a TIM catalyst after calcination is a little bit complicated, which is composed of a mild diffraction of the Al_2O_3 phase [37.5, 45.7, 67.0°; JCPD 77-0396], a strong diffraction of the NiO phase [37.2, 43.2, 62.8°; JCPD 89-3080], and a weak diffraction of the metallic Ni phase [44.3, 51.7, 76.3°; JCPD 70-1849]. Evidently, nickel oxide cannot be completely reduced under the reduction conditions employed, which is related to the strong interaction between the nickel species and the alumina carrier. In comparison, the diffraction pattern of the IRM catalyst is very simple. Only the diffractions of the metallic Ni and Al_2O_3 phases are visible. Clearly, the nickel oxide is more reducible, implying the lower interaction between the Ni species with the alumina carrier.

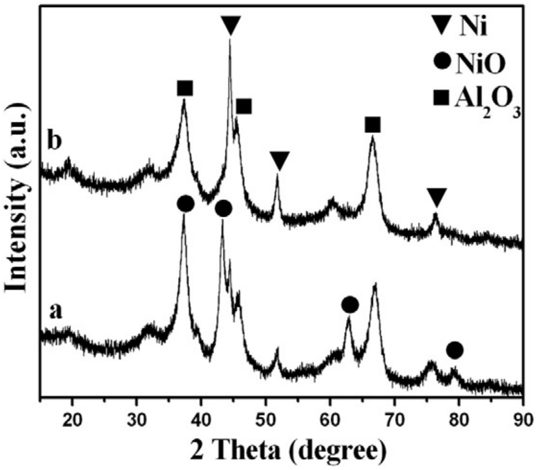

Fig. 1. XRD patterns for Ni/Al_2O_3 catalysts, a) reduced TIM catalyst (reduction condition: T = 600 °C, hydrogen flow rate: 40 ml/min, 3 h), b) IRM catalyst.

In the preparation of the traditional TIM catalyst, the catalyst precursor is exposed to an oxidizing atmosphere and temperature for a long time, leading to the strong interaction between the Ni species (oxide form) and the alumina carrier. In the process of the IRM catalyst preparation, the catalyst is totally prepared in situ and only the impregnation and reduction steps are involved. No calcination is involved and the catalyst is not exposed to air, which, clearly, alleviates the strong interaction between the Ni species and the alumina carrier, resulting from the incorporation of Ni^{2+} into the alumina lattice during the calcination process [29].

Metal dispersions in TIM and IRM catalysts are measured using the H_2-TPD technique. The hydrogen desorption profiles are present in Fig. 2. The profile of an IRM catalyst is composed of the overlapping of a main peak centered at 441 °C and a small shoulder centered at 563 °C, indicating that two types of nickel species exist on a catalyst surface. In comparison, the profile of the TIM catalyst is composed of the overlapping of three peaks centered at 369, 450, and 591 °C, indicating the existence of three types of nickel species. Evidently, the Ni species on the IRM catalyst surface is more uniform than that of the TIM catalyst. The metallic Ni species in the IRM catalyst may directly be formed from the reduction of nickel nitrate, while the metallic Ni species in the TIM catalyst are formed from the reduction nickel oxide, which may lead to the formation of the different Ni species on alumina.

The metal dispersions of IRM and TIM catalysts are 14.9 and 5.6%, respectively. Much more metallic Ni species appear on surface of the IRM

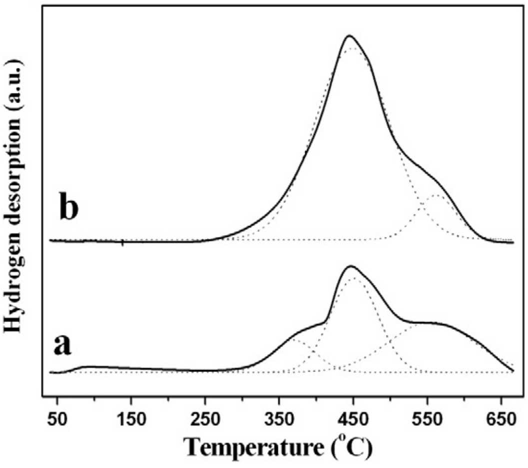

Fig. 2. H_2-TPD profiles for Ni/Al_2O_3 catalysts, a) reduced TIM catalyst, b) IRM catalyst.