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Characterization and catalytic properties of Ni/SiO_2 catalysts prepared with nickel citrate as precursor

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ABSTRACT

The Ni/SiO_2 catalysts were prepared with nickel citrate precursor by using incipient-wetness impregnation method, characterized by FT-IR, UV-Raman, TG-DTA, XRD, HR-TEM and H_2-TPR, and tested in the reaction of methane reforming with CO_2 and O_2 to produce syngas. The highly-dispersed Ni particles (~7 nm) on support SiO_2 were observed by TEM. FT-IR results indicated that there existed interaction between nickel citrate precursor and SiO_2. H_2-TPR results demonstrated that, this interaction was enhanced by calcination at high temperature to form strong NiO–SiO_2 interaction, and the strong interaction was recovered after repeating oxidation–reduction–oxidation cycle at 700 °C. As a result, the Ni/SiO_2 catalysts showed a good activity and super stability without sintering of nickel particles during 36 h reaction on stream.

1. Introduction

As possible substitute for noble metals catalysts, the Ni-based catalyst is recently recognized as one kind of the most promising catalysts [1,2] because of its low cost, high activity for many catalytic reactions, such as hydrogenation of olefins and aromatics [3], methane reforming [4] and water-gas shift reaction [5]. However, coking and deactivation in hydrocarbon involved reactions, mostly due to low dispersion of nickel on support, are the greatest obstacles for Ni-based catalyst to practical application [6–10]. Many researches have been focused on the selection of promoters (alkaline metal oxides, alkaline earth metal oxides, rare earth metal oxides) [10–14], supports [2,15–17] and preparation methods [18–23] to improve the catalytic performance of Ni-based catalyst.

The Ni-based catalyst synthesis method, which will result in different structural and textural properties, plays an important role in the catalytic performance. Therefore, numerous methods, including precipitation, homogeneous deposition–precipitation and sol–gel techniques, have been developed to enhance the performance of Ni-based catalysts [16–24]. However, all the above methodologies mentioned are too complex or expensive to scale up in industry. The incipient wetness impregnation (IWI) is the most extensively used method [25–28] due to its simplicity in practical execution on both laboratory and industrial scales, in addition to its facility in controlling the amount of the load of the active ingredient.

In general, the choice of the precursor salt is crucial since it has a significantly influenced on the characteristics of the resulting catalysts, such as metal dispersion, average particle size and particle size distribution [29–31], which are key factors affecting the catalytic behavior. Nickel nitrate is the precursor most often used in the preparation of Ni-based catalyst owing to its low cost, high solubility in water and effortless decomposition at moderate temperatures. However, it is easy to agglomerate over the support upon calcination, thus resulting in poorly dispersed metal particles after reduction, and also their weak interaction with the porous support system [32]. Furthermore, the toxic gas of NO_x produced by decomposition of the nitrate is a serious environmental concern [32]. These problems have provided an impetuousity to the search for alternative precursors of nickel nitrate. Multicarboxylic nickel precursor, such as nickel citrate, nickel EDTA, is a good choice [27,28]. In particular, the citrate precursor method is a simple and commercially viable chemical route, which decomposes into CO_2 and H_2O. It achieves the atomic-level mixing of the constituent metal ions, thus resulting in homogeneous metal particles with smaller size and high dispersion [33–36]. Recently, the citrate precursor has already been successfully applied to prepare highly dispersed supported metal catalysts [27,28,37–40]. However, the mechanism of citrate on supported catalysts is not clear. In this

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paper, Ni/SiO_2 catalysts with nickel citrate as precursor using IWI were prepared and characterized by TG-DTA, HR-TEM, IR, UV-Raman, XRD and H_2-TPR techniques in order to reveal the relationship between synthesis, properties and catalytic performances.

2. Experimental

2.1. Catalyst preparation

The Ni/SiO_2 catalysts were prepared with IWI using nickel citrate as precursor according to our previous works [27,28], which are introduced briefly as following procedures. An equal molar ratio of nickel carbonate and citric acid were mixed together. Then de-ionized water was added into the mixture, and heated at ~100 °C until nickel carbonate was dissolved to form a green and transparent solution. The nickel citrate precursor was designated as NiCA. After impregnation, the samples were dried at 100 °C for 12 h and subsequently calcined in air at 700 °C for 4 h. Unless otherwise stated, the loading of Ni was 3 wt%, and the calcination temperature was 700 °C. The Ni/SiO_2 catalyst was designated as 3NiSC.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM) images were recorded on a Philips-FEI transmission electron microscope (Tecnai G2 F30 S-Twin, The Netherlands), operating at 300 kV. Samples were mounted on a copper grid-supported carbon film by placing a few droplets of ultrasonically dispersed suspension of samples in ethanol on the grid, followed by drying at ambient conditions.

FTIR spectra were measured using a Nicolet 560 spectrometer equipped with a MCT detector. The samples were tabletted to thin discs with KBr.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a PERKIN ELMER-TAC7/DX with a heating rate of 10 °C/min under oxygen (99.99%, 20 ml/min). The samples were pretreated with oxygen flow at 383 K for 1 h.

UV-Raman spectra were carried out with a Jobin Yvon LabRam-HR800 instrument, using 325.0 nm Ar^+ laser radiation. The excitation laser was focused down into a round spot approximately 2 μm in diameter. The resolution was 4 cm^{-1} and 1000 scans were recorded for every spectrum. The catalysts were ground to particle diameters <150 μm before analysis.

X-ray powder diffraction (XRD) patterns of samples were obtained with an automated power X-ray diffractometer (Rigku-D/max-2550/PC, Japan) equipped with a computer for data acquisition and analysis, using Cu Ka radiation, at 40 kV and 300 mA. The reduced samples were prior reduced at 700 °C for 1 h and cooled to room temperature in hydrogen atmosphere, but the fresh samples were used directly after calcined in air at 700 °C for 4 h. All the samples were ground to fine powder in an agate mortar before XRD measurements.

H_2-temperature-programmed reduction (H_2-TPR) experiments were performed in a fixed-bed reactor (I.D. = 4 mm). 50 mg samples were used and reduced under a stream of 5% H_2/N_2 (20 ml/min) from 50 °C to 800 °C with a ramp of 7 °C/min. Hydrogen consumption of the TPR was detected by a TCD and its signal was transmitted to a personal computer.

The experiments for reduction–oxidation cycle (redox) performance were performed as follows. The catalysts were pretreated with H_2 flow at 700 °C for 1 h, and then were cooled down to room temperature and reoxidized in O_2 at different temperature for 1 h. The re-oxidized samples were then performed H_2-TPR experiments as above.

2.3. Catalytic reaction

A fluidized-bed reactor comprised of a quartz tube (I.D. = 20 mm, H = 750 mm) was adopted to measure the catalytic performance of the prepared catalyst under atmospheric pressure at 700 °C. Prior to reaction, 2 ml of catalyst was pre-reduced at 700 °C for 60 min under a flow of pure hydrogen at atmospheric pressure. A reactant gas stream that consisted of CH_4, CO_2 and O_2, with a molar ratio of 1/0.4/0.3, was introduced to the reactor with a gas hourly space velocity (GHSV) of 9000 h^{-1}. The flow rate of feed gases was controlled by mass flow controllers. The effluent gas cooled in an ice trap was analyzed with an online gas chromatography equipped with a packed column (TDX-01) and a thermal conductivity detector. The conversion and the selectivity were calculated as the literature [41].

3. Results and discussion

3.1. Catalyst characterization results

3.1.1. TEM analysis

The shape, size and morphology of the single-phase particles were examined by direct observation via TEM. The TEM images of 3NiSC catalysts given in Fig. 1a demonstrated that the Ni particles were approximately spherical in shape and highly dispersed on the support of SiO_2. The particle size histogram from sampling of about 200 particles from different TEM images was presented in Fig. 1c. The particle size values were distributed in a range of 3.4–19.9 nm with the average size around 7.4 nm. Most of the nickel particles were smaller than 8 nm. Fig. 1b high-resolution transmission electron microscopy exhibited the lattice spacing of 0.2026 nm between the adjacent planes, from which the lattice fringes of metal nickel (1 1 1) planes were confirmed [42].

3.1.2. FT-IR analysis

The FT-IR spectra of 3NiSC before calcination and NiCA precursor were illustrated in Fig. 2. Two intense bands of NiCA centered at 1589 cm^{-1} and 1408 cm^{-1} were ascribed to $V_{as}COO^{-1}$ and V_sCOO^{-1} [43,44], respectively. After NiCA being impregnated on SiO_2, the position of the two bands of NiCA shifted to higher wavenumber about 1610 cm^{-1} and 1420 cm^{-1}, respectively, which might be contributed to the interaction between nickel citrate and support SiO_2 through hydrogen bonds. Upon gradual removal of the solvent, the nickel citrate chelate complexes formed a gel-like phase, which might interact weakly but sufficiently with support SiO_2 through hydrogen bonds, thus resulting in red shift in the above peaks position of 3NiSC [45]. Furthermore, the rapid increasing of the viscosity of the solution upon drying due to gelation would inhibit redistribution of the impregnation solution [45]. The above two interdependent phenomena were in favor of a uniform distribution of Ni over the support bodies, thus leading to highly-dispersed active nickel metals on SiO_2.

3.1.3. Thermal analysis

In order to investigate the formation of NiO from precursor, thermal analysis of 3NiSC before calcination was carried out (showed in Fig. 3). The extra water should be removed by holding the precursor under O_2 at 110 °C for 1 h. The thermal-oxidation degradation of the dried 3NiSC consisted of two main steps. The first weight loss at 110–290 °C region (13.1 wt%) in TG, associated with a differential peak at around 225 °C in DTG curve is probably due to the dehydration of 3NiSC. The second large weight loss at region of 290–350 °C (14.7 wt%) in TG, accompanied with a intense exothermic peak around 340 °C in DTA, was attributed to thermoxidative degradation of nickel-citrate. This decomposition step exhibited a differential peak around 335 °C in DTG profile.