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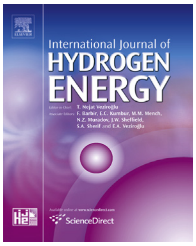

Highly dispersed supported metal catalysts prepared via *in-situ* self-assembled core-shell precursor route

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ABSTRACT

Preparation of highly dispersed supported metal catalysts, which has high activity and selectivity, is still one of the main challenges for catalysis science. Highly dispersed supported metal catalysts via an economical incipient wetness impregnation method by impregnation of a small amount of oleic acid mixed with metal nitrate on catalyst support is reported herein. XRD, TEM(STEM), SEM, XPS, FTIR and EXAFS results revealed that the small amount of oleic acid and metal nitrate solutions would *in-situ* self-assemble to form core–shell precursors (metal nitrate species as core and metal oleate as shell), and metal agglomeration during heat treatment was drastically prevented by the steric hindrance of the shell structure. Therefore, the novel and facile method was named as *in-situ* self-assembled core–shell precursor route. The effectiveness of this method was attested by copper and nickel on silica catalysts. Compared to the conventional preparation method, the as-prepared highly dispersed metal catalysts of Cu/SiO_2 and Ni/SiO_2 exhibited excellent catalytic activities for water gas shift reaction and carbon dioxide reforming of methane at high temperatures.

Introduction

Catalysis is an innovative and powerful technology to solve many of today's energy and environmental issues. Particularly, supported metal catalysts hold great importance in catalysis researches and industrial applications [1–4]. Highly dispersed supported metal catalysts are greatly sought after since a decrease in the supported particle size is accompanied by an increase in the surface area of active phase and a consequent enhancement in the catalytic activity. In the past decades, tremendous advances have been achieved in the

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preparation of highly-dispersed metal catalysts using different methodologies, such as sol–gel method [5–11], co-precipitation or deposition precipitation method [12–18] and ion exchange or strong electrostatic adsorption (SEA) [19,20]. Although all of the above-mentioned methods have been successfully adopted in some applications, numerous disadvantages such as high cost and difficulty in scaling up hindered application of these methods in the industrial setting.

Impregnation method, in particular incipient wetness impregnation, is highly desirable due to its practical simplicity and its minimal generation of waste streams. In a bid to improve the metal dispersion on support, various metal precursors and organic metal compounds (acetate [21], citrate [22,23] and acetylacetonate [24,25]), have been utilized. Recently, Ni(1,5-cyclooctadiene)$_2$ was reacted with octylsilane to form nickel-silicide colloids [$Ni_xSi-C_8H_{17}$] in the presence of H_2, and was used as a precursor to prepare highly dispersed supported nickel catalysts [26]. Besides, a versatile method involving a surface organometallic chemistry (SOMC) route that uses mono(η^3-allyl)nickel complex as precursors to prepare supported small size nickel nanoparticles (*ca.* 1–3 nm) with narrow size distribution was reported [27]. However, the organometallic compounds mentioned above are not only costly but also have low solubility in aqueous solution and/or highly sensitive to moisture or air, rendering them difficult to be applied in industry. Due to their inherent advantages, such as low cost, high solubility in water and ease of anion removal, metal nitrates are widely utilized as precursors for the preparation of supported metal catalysts. However, the drawback of using metal nitrate during the preparation of supported metal catalyst lies in the wide distribution of metal particle size which falls between 1 and 100 nm. The ease of agglomeration of metal precursors during the drying and calcination steps has been attributed for the cause of this phenomenon [28]. Interestingly, the de Jong group found that the metal dispersion could be enhanced by using an NO/He mixture atmosphere during catalyst calcination [28,29]. It was revealed that NO could promote nearly complete hydrolysis of metal nitrate to hydroxynitrates, which possessed a reduced mobility to agglomerate upon decomposition that occurred between 100 °C and 150 °C [28]. In addition, Stucky et al. also reported another noteworthy method to prepare oxide-supported metal nanoparticle in which the weak interaction between presynthesized hydrophobic metal particles and oxides supports was utilized to assemble the nanoparticles onto the oxides surface [30]. However, this method cannot be used in protic solvents and large scale production. Hence, there remains a tremendous barrier to design a more general and simplistic method for preparation of highly dispersed, supported metal catalysts. Precedently, we have reported a method to prepare highly-dispersed and stable Cu/SiO$_2$ and Ni–La$_2$O$_3$/SiO$_2$ catalysts using the incipient wetness impregnation (IWI) in the presence of a small amount of fatty acids and metal nitrate [31,32]. Herein, XRD, TEM, SEM, XPS, FT-IR and EXAFS techniques are applied to elucidate the promoting mechanism of oleic acid on the dispersion of Ni/SiO$_2$ and Cu/SiO$_2$ catalysts. Catalytic activities of the prepared Ni/SiO$_2$ and Cu/SiO$_2$ catalysts were measured using carbon dioxide reforming of methane and water gas shift reaction, respectively.

Experimental section

10%Cu/SiO$_2$ catalyst preparation and water gas shift reaction conditions

Cu/SiO$_2$ catalysts promoted with oleic acid (OA) were prepared with incipient wetness impregnation, with a copper loading of 10wt.%. Firstly, 2.1 g copper nitrate (from Merck) was dissolved in D.I. water, and then different amount of oleic acid (from Sigma–Aldrich) was added into the solution. At last, 5 g spherical silica (from Kanto Chemical Co.: specific surface area = 753 m^2/g, mean pore size = 7.5 nm) was introduced into the above solution. The samples were subsequently impregnated at room temperature for >6 h and then dried overnight at 100 °C. The above dried samples were calcined at 450 °C for 4 h. The amount of OA was calculated as molar ratio of $X = n_{OA}/n_{Cu}$, and X was adopted as 0, 0.05, 0.25, 0.5, and 1.0, respectively. And the 10%Cu/SiO$_2$ prepared with different X was designated as 10%Cu/SiO$_2$/X. To investigate the catalytic performance of the prepared catalysts at 300 °C, the Water Gas Shift Reaction (WGSR) was used as a probe reaction. The feed composition, with a total flow rate of 50 ml/min, was as follows: 5 mol.% CO, 25 mol.% H_2O, and He balance. The effluent gases were analyzed by an HP-GC equipped with a Hayesep D column. All catalysts were reduced at 300 °C for 1 h prior to the onset of WGSR.

5%Ni/SiO$_2$ catalyst preparation and dry CO$_2$ reforming of CH$_4$ reaction conditions

The 5%Ni/SiO$_2$/X catalysts were prepared similar to those of 10%Cu/SiO$_2$. The $X = n_{OA}/n_{Ni}$ ratios adopted were 0, 0.05, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0, respectively. Calcination was conducted at 700 °C for 4 h in air atmosphere.

The dry CO$_2$ reforming of CH$_4$ (DRM) reactions were carried out in a quartz reactor. The catalyst under study was loaded and packed in the middle of the quartz-tube using quartz wool which was inert in the reaction. Under atmospheric pressure, the catalyst was heated from the initial room temperature to a reaction temperature of 700 °C at a rate of 20.0 °C/min in a horizontal electric furnace. The Gas-Hourly-Space-Velocity (GHSV) was 72,000 ml h^{-1} g (cat.)$^{-1}$. Additionally, high purity feed gases (99.99%) were controlled by mass flow rate controllers and a molar ratio of $CH_4/CO_2/N_2 = 1/1/1$ was adopted. Prior to the catalytic reaction, the catalysts were reduced in-situ in a H_2 atmosphere (purity = 99.99%) at 700 °C for 1 h and 0.05 g of catalyst was used in each catalytic test. To remove any moisture from the effluent gas stream, a cold trap was employed to condense the moisture prior to gas analysis by an on-line gas chromatograph (GC). Effluent gas from the reactor was analyzed by an Agilent HP-GC equipped with two columns of 5 Å and Porapak Q. The nitrogen in the reactants acted as an internal standard.

Copper (nickel) oleate synthesis

The copper oleate synthesis follows the method reported in literature [33]. Typically, 0.85 g (5 mM) CuCl$_2$.2H$_2$O (Fisher Chemical, >99%) was dissolved in a mixture solution