



Research article

Effect of synthesis and activation methods on the catalytic properties of silica nanospring (NS)-supported iron catalyst for Fischer-Tropsch synthesis



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ABSTRACT

A nanostructured iron (Fe) catalyst for Fischer-Tropsch synthesis (FTS) was prepared and evaluated using a silica nanospring (NS) support. FTS offers an approach of producing biofuels from synthesis gas (syngas) produced via biomass gasification. The Fe/NS catalysts were prepared using three different methods: (i) incipient wetness impregnation, (ii) precipitation and (iii) modified sol-gel, in order to obtain different sizes of deposited Fe nanoparticles on the NS support and investigate the influence of particle size on FTS. The Fe decorated catalysts were calcined and then activated with either H₂, CO or H₂ + CO mixture. The prepared Fe/NS catalysts were characterized before the FT reaction by BET surface area, X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) in order to find correlations between physico-chemical properties of catalysts and catalytic performance. The decoration of Fe nanoparticles of different sizes onto NS using the various methods ranged from 1.7 to 10 nm. The FTS performance was also evaluated in a quartz fixed-bed microreactor (H₂/CO of 2:1, 270 °C) and the products trapped and analyzed by GC-TCD and GC-MS to determine CO conversion and reaction selectivity. These results show that the highest CO conversion (76.6%) and a wide distribution of light hydrocarbon (C₆ to C₁₄) were obtained for Fe/NS catalyst prepared by impregnation and activated with CO after 12 h of the FT reaction.

1. Introduction

Fischer-Tropsch synthesis (FTS) has been recognized as one of the most promising alternative technologies in converting syngas derived from coal, natural gas and biomass into liquid transportation hydrocarbon fuels and chemicals. Over the years, the FTS process is still subject to further research and development to improve the efficiency of FTS technology in order to produce a wide variety of hydrocarbons products [1]. In order to improve the catalytic performance of FTS catalysts, active metal catalysts such as iron (Fe) and cobalt (Co) are generally supported on conventional support materials such as SiO₂, Al₂O₃, and TiO₂ gels [2,3]. Although there are many positive sides of FT catalysts supported on conventional substrates, there are also some technical and economic challenges that still need to be overcome, including strong metal oxide-support interaction, the price of the active metal (Ru and Co), catalyst lifetime and catalyst deactivation [4,5]. All these limitations will either inhibit the FT catalytic activity or increase the cost of fuel production. It is therefore necessary to find efficient ways to overcome these obstacles and challenges. Approaches for

overcoming these limitations are to change the support, addition of promoters, synthesis and activation methods. These will have a significant influence on the metal dispersion, particle size, minimizing the cost of the catalyst, reduction behavior, catalytic activity and FT selectivity [5,6].

Although a number of studies were carried out on the effect of synthesis and activation methods of different Fe catalyst on the FTS performance [7,8], further research is still needed to develop new FT catalysts that improve the quality and value of FTS products. The synthesis of the Fe catalysts have been studied extensively and many synthesis catalyst methods such as sol-gel (-S), precipitation (-P) and incipient wetness impregnation (-I) have been successfully applied in the synthesis of Fe-based catalysts [7,9–12]. However, the synthesis methodology plays a key role in controlling the morphology, catalyst particle size, size distribution and surface area [13,14]. For example, Tasfy et al. [7] reported that the average Fe nanoparticle size over SiO₂ was smaller when prepared by the impregnation catalyst synthesis method, as compared to the precipitation method. Sarkari et al. [10,11] investigated the effect of impregnation and co-precipitation methods of

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Fe/Ni/Al₂O₃ catalyst on the FTS performance. They found that the impregnated catalyst had higher activity and higher selectivity to light olefin and C₅ + products than the co-precipitated catalyst.

Catalyst activation methods of supported and unsupported iron oxide catalysts have been investigated in order to improve the performance of FTS [15]. The phases of the iron catalysts are typically present as metallic iron (α -Fe), Fe oxides, and Fe carbides (Fe_xC_y) during the FT reaction [16]. In FTS, the iron oxide catalyst is inactive, so it is necessary to change the oxidation state of iron into an active phase (metallic Fe or iron carbides) for the FT reaction to occur [16,17], and depending on the activation agents used. The activation of an iron-based catalyst by common activation agents (i.e., H₂, CO or H₂ + CO mixture) has a significant influence on the FTS activity, selectivity, and the surface phase composition [15,17,18]. Several studies have reported that activation of iron oxide catalyst with CO showed a superior FTS activity compared to H₂ and H₂ + CO mixture. For example, Luo et al. [17] studied the activation of low α -iron catalyst with three different activation agents (i.e., H₂, CO or H₂ + CO mixture). They found that higher CO conversion was obtained when activation with CO and syngas. Bian and co-workers [16] studied the activation effect of CO and H₂ on precipitated Fe₂O₃ catalyst and concluded that the CO activation produced higher catalytic activity for FT synthesis than the H₂-activated iron catalyst. They also found that the surface area of the H₂-activated iron catalyst showed a small decrease compared with that of the CO-activated iron catalyst. Similar results were obtained by Ding et al. [19] with a Fe-Mn-K-SiO₂ catalyst. Furthermore, they reported that the CO activated catalyst presented the highest initial activity compared to the H₂ and syngas activated catalysts.

Several conventional catalyst support materials (SiO₂, Al₂O₃, and TiO₂) have been extensively used and investigated as supports for FTS catalysts. However, unconventional catalyst support materials such as 1-dimensional (1D) nanomaterials (e.g., carbon nanotubes (CNTs), tin oxide nanowires (SnO₂) and carbon nanofibers (CNFs)) have recently attracted considerable attention as potential supports in FTS catalysts [8]. This is mainly due to their unique structure, properties (e.g. high surface area and high thermal stability) and ability to improve the performance of the FTS catalyst.

Silica nanosprings (NS) is a new 1D support material and has been recognized as meeting the criteria of supports because they have (i) high surface area (300 m²/g), (ii) high thermal stability (up to 1000 °C), (iii) easy to grow, and (iv) can be grown in various surfaces [20]. Up to now, NS is a relatively new support material for FTS, hence, only two studies have used NS as a FT support [21,22]. The first proof of principle study of NS as a new high surface area support for Co-FTS catalyst was to produce hydrocarbons from the hydrogenation of [21]. A subsequent study showed that the Co-NS catalyst was not fully activated/reduced at 409 °C under H₂ prior to FTS evaluation and, where H₂-TPR and XPS studies showed that full activation required H₂ reduction at 609 °C, which subsequently improved CO conversion [22].

In the present study, three different 1D iron-NS catalysts were prepared to obtain differing Fe particle size distributions using three different methods: incipient wetness impregnation, precipitation and modified sol-gel. The catalysts were calcined and then activated with either H₂, CO or H₂ + CO mixture. The catalysts were characterized by a combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), H₂ and CO temperature programmed reduction (H₂-TPR, CO-TPR), Infra-red (IR) spectroscopy and surface area measurements. The effect of synthesis method and activation conditions on catalytic performance of 1D Fe/NS catalysts for FTS were studied.

2. Experimental methods

2.1. Catalyst preparation

NS were prepared in 0.5 g batches according to Wang et al. [23].

Fe/NS catalysts with total Fe loading of 15% were prepared using three different methods: (a) incipient wetness impregnation; (b) precipitation and (c) modified sol-gel.

(a) Incipient wetness impregnation

NS (75 mg) were dispersed in ethanol (15 ml) to which a solution of Fe (NO₃)₉H₂O (100 mg in 15 ml water) was added drop-wise under ultrasonication for 15 min at room temperature. The mixture was stirred at 80 °C for 24 h, air dried at 110 °C for 24 h, and then calcined in air at 500 °C for 5 h and called Fe/NS-I [7,24,25].

(b) Precipitation method

(100 mg in 15 ml water), and heated to 70 °C. The mixture was precipitated using 0.2 M sodium hydroxide to obtain a pH of 9–10 at 80 °C. The precipitate was aged in this medium for 2 h. The aged suspension was filtered and then washed with water until neutral. The precipitated solid was dried at 110 °C overnight, calcined in air at 600 °C for 5 h, ground and sieved, and called Fe/NS-P [7,25].

(c) 2-Step sol-gel method

Fe nanoparticles without NS were prepared by sol-gel method using Fe (NO₃)₉H₂O (1.5 g in 60 ml water) to which citric acid (3 g) was added under ultrasonication for 2 h at room temperature. The solution pH was adjusted to 10 using 1 M NaOH solution. The mixture was heated overnight at 70 °C resulting in a viscous brown gel being formed. The gel was then dried at 110 °C for 8 h and calcined in air atmosphere at 400 °C for 5 h [3]. The second step was to disperse the magnetite nanoparticles (20.4 mg) in water (10 ml) and then mixed overnight at room temperature with a suspension of NS (50 mg) in ethanol (10 ml). The mixture was dried at 110 °C for 12 h and then calcined at 600 °C in air atmosphere for 4 h and called Fe/NS-S [4].

2.2. Catalyst characterization

The reduction and carburization behavior of the calcined catalysts (30 mg) were performed by H₂-TPR and CO-TPR using a ChemiSorb 2720 instrument (Micrometrics, USA) equipped with a TCD detector. The TCD was calibrated by the reduction of CuO (20 mg, 99.99%) between 25 and 500 °C. Before running each TPR experiment, the catalyst was flushed with N₂ (30 ml/min) at 150 °C for 1 h to remove the surface impurities and then cooled to 25 °C. H₂-TPR and CO-TPR experiments were conducted in a 10 vol% H₂ or 5 vol% CO, respectively in N₂ atmosphere with a total flow rate of 30 ml/min. The temperature was ramped from 25 to 1000 °C for H₂-TPR and from 65 to 700 °C for CO-TPR both at a heating rate of 10 °C·min⁻¹. The specific surface area (S_{BET}) of all degassed (220 °C for 30 min) catalysts (60–80 mg) were measured using an N₂ adsorption-desorption isotherm at –196 °C on a Micromeritics ChemiSorb 2720 instrument. The FT-IR spectroscopic analysis of the catalysts (10% mixed with KBr) was obtained in the diffuse reflectance mode using a Thermo Nicolet Avatar 370 DTGS spectrometer.

The crystallographic information of the calcined catalysts was studied by XRD on a Siemens D500 powder diffractometer with Cu/ α (λ = 0.154 nm) radiation. Diffraction intensities were recorded from 10°–80° (2 θ value) with 0.01° step using a 1 s acquisition time per step. The average crystallite size of iron oxides was calculated using the diffraction peaks according to the Scherrer equation [26]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite in nm, k is shape factor (for spherical shape particles, k = 0.9), λ is the wavelength of X-ray (λ = 1.54 Å), β is line broadening at half the maximum intensity (FWHM) in radians, θ

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