Effect of preparation methods on activation of cobalt catalyst supported on silica fiber for Fischer–Tropsch synthesis

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HIGHLIGHTS

- Silica fibers (SF) were prepared by sol–gel method and electrospinning technique.
- Four different preparation methods of cobalt-based catalysts are reported.
- Catalytic activity depends on Co particle size and reducibility of the catalyst.
- The Co/SF catalyst prepared by the SEA method showed the highest activity for FTS.

GRAPHICAL ABSTRACT
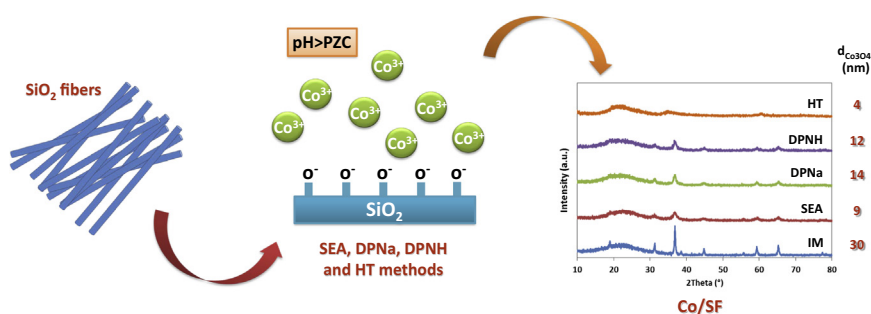
ABSTRACT

Silica fibers (SF) have been synthesized by facile combination of a sol–gel method and electrospinning technique and investigated as supports of cobalt catalysts for Fischer–Tropsch synthesis (FTS). Tetraethyl orthosilicate (TEOS) was used as precursors for the production of silica fibers. The cobalt supported on silica fibers (Co/SF) catalysts were prepared with the impregnation (IM), strong electrostatic adsorption (SEA), deposition precipitation (DP), and hydrothermal synthesis (HT) method and characterized by N_2 adsorption, SEM, TEM, XRD, EDX, H_2-TPR and H_2-chemisorption. The results showed that the preparation methods significant affected the catalytic activity of Co/SF catalyst. The catalyst prepared by the SEA method showed the highest catalytic activity for FTS reaction, and their catalytic activities were varied in the order of SEA > DP > IM $\gg$ HT. The XRD analysis showed that the Co_3O_4 particles on the Co/SF catalyst prepared by SEA method (9 nm) were smaller than those on catalyst prepared by IM method (30 nm). The size of the Co_3O_4 particles was controlled by the preparation method, with small particles formed in catalyst prepared by SEA, DP and HT method. The excellent catalytic activity of Co/SF-SEA may be attributed to the smaller size of cobalt particles and higher cobalt dispersion on this catalyst.

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1. Introduction

The Fischer–Tropsch synthesis (FTS) is an industrialized process in the production of liquid fuels and chemicals from syngas. In the FTS reaction, syngas is converted into liquid fuel via catalytic surface polymerization which leads to a large variety of products such as paraffins, olefins, alcohols and aldehydes [1,2]. Cobalt based catalysts have been found to be most suitable for the higher hydrocarbon in FTS synthesis [1,3]. The performance of the cobalt catalyst in FTS reaction is greatly influenced by the catalyst preparation method. The variables include suitable support, deposition method

of the metal precursor, catalyst promoter, and the subsequent thermal treatments [4,5]. The reactivity in FTS is correlated to the number of cobalt metallic particles exposed to the syngas molecules. This factor depends on the cobalt loading, dispersion of cobalt species and its reducibility. Hence, an ideal supported catalyst would have uniformly distributed cobalt species that undergoes complete reduction, forming cobalt metallic nanoparticles at optimum size of 6–8 nm [6]. FTS catalysts have been prepared by various methods such as impregnation (IM) [4,7,8], precipitation [9,10], colloidal [11], strong electrostatic adsorption [12,13], and microemulsion method [14,15].

Silica, as a common support used in the catalysts of Fischer–Tropsch synthesis, presented the characteristics of a higher surface area, porosity, stability and weaker metal–support interaction than aluminum as support [16]. However, the weak interaction between cobalt and silica in silica-supported catalysts favors the reduction of cobalt precursor and promotes agglomeration of supported cobalt particles, reducing the dispersion of supported cobalt and the numbers of active sites [17,18]. One-dimensional (1D) nanostructure such as nanofibers, nanorods, nanotubes and nanobelts are receiving increasing attention because of their large length to diameter ratio. The fibers have also been demonstrated and have many potential applications in various areas such as tissue engineering, catalysis, sensing, as well as fabrication of composite materials, supercapacitors, and tubular structures [6,14,19–21]. These materials have been proven to be the promising catalysts that combine the advantage of shape selectivity with the efficient mass transport.

The incipient wetness impregnation method is a commonly used method for preparing cobalt and iron catalysts. Impregnation (IM) is a method of cobalt deposition on porous support in which a dry support is contacted with a solution containing dissolved cobalt precursors [3]. The method of strong electrostatic adsorption (SEA) is a simple, rational method for the preparation of catalysts. The SEA method is based on an electrostatic mechanism in which the functional groups (typically hydroxyl) on the support surface can be protonated and deprotonated and thus positively or negatively charged as a function of pH (relative to the point of zero charge [PZC]). At the pH of strongest interaction, oppositely charged metal coordination complexes adsorb in a well dispersed monolayers. For example, with 5% (w/w) loading of Co(III) hexamines precursor solution, 100% cobalt uptake was achieved in pH range of 8.8–9.9. The narrow particle size distribution of cobalt was obtained with an average particle diameter of 5.2 nm [13]. The deposition precipitation (DP) method is convenient and is used for producing commercial gold supported catalysts [22–24]. The DP method allowed to produce small gold particles size, and highly active gold catalysts in various reactions. The required amount of the precursor salt is dissolved in deionized water and added to the support with constant stirring followed by the addition of precipitating agent i.e. ammonia and the resultant slurry is aged for about 12 h. The precipitate is dried and then calcined [25].

As a catalyst support, SF has many advantages such as resistance to acids or bases and stability at high temperatures in inert or reducing atmospheres, which allows the catalyst properties to be tailored for specific needs. However, the non-porous properties of SF and weak metal-support interaction of SiO_2 can lead to increase particle size and decrease the dispersion of metal. In this work, silica fiber was synthesized by electrospinning technique and used as the support for cobalt catalyst. The effects of the preparation methods on the physicochemical properties of cobalt oxide supported on SF catalyst were studied, and its catalytic performance was tested for the FTS. Each catalyst was characterized by N_2 physisorption, X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscope (SEM), transmission electron microscopy (TEM), H_2-chemisorption and hydrogen temperature programme reduction (H_2-TPR) analyses, while its performance in the FTS reaction was evaluated in a fixed-bed reactor. The Co supported on non-porous SF catalysts with higher BET surface areas and smaller Co_3O_4 crystallite diameter could be obtained by strong electrostatic adsorption (SEA) and deposition precipitation (DP) method which is based on an electrostatic mechanism on the support surface. The Co/SF which prepared by SEA method had Co_3O_4 particle size of 9 nm and exhibited the highest CO conversion.

2. Experimental section

2.1. Catalyst preparation

2.1.1. Preparation of silica fiber support

Preparation of silica sol solution: Based on conventional sol–gel process, tetraethyl orthosilicate (TEOS, Fluka, 98.0%), ethanol (Analar Nor Mapur, 99.8%), de-ionized (DI) water, and hydrochloric acid (HCl, CARLO ERBA, 37.0 wt%) at a molar ratio of 1:2:2:0.01, respectively, were used as starting material. First, TEOS was mixed with DI water and stirred for 5 min. Then, HCl and ethanol were added under continuous stirring for another 5 min. The precursor solution was heated to 55 °C and stirred for 30 min before it was cooled to room temperature.

Electrospinning process: All electrospinning experiments were carried out at room temperature in air. High voltage DC power supply was used to generate potential differences of between 10 kV and 20 kV. The silica sol solution was fed from a syringe to a needle (spinneret with a hole diameter of 0.25 mm) and the flow rate was controlled using a syringe pump (KDS 100, KD Scientific, Co.), the achievable flow rate was 10 mL/h. A clamp connected with high voltage power supplier was attached to the syringe. As grounded collector, a piece of aluminum foil was placed towards the tip at the distance of 10, 15 and 20 cm. The electrospun fibers were collected, then dried at 110 °C overnight and then calcined at 600 °C for 4 h.

2.1.2. Preparation of the silica fiber supported cobalt catalyst

The cobalt supported on silica fiber (Co/SF) catalysts were prepared by a wet impregnation (IM), strong electrostatic adsorption (SEA), deposition precipitation (DP) with sodium hydroxide (DPNa) or ammonia (DPNH) solution and hydrothermal (HT) method designated as Co/SF-X, where X stands for preparation method of catalyst. The theoretical loading of Co was 10 wt%.

The SEA samples were prepared as follows: silica fiber was added to DI water and used ammonia solution (28%) to adjust the pH to 12. Then $Co(NO_3)_2$ solution was added into the mixture. After that, the solid was filtered and washed with DI water until pH 7 for the eluate solution. The DP samples were prepared as follows: $Co(NO_3)_2$ was dissolved in DI water and NaOH solution (1 M) or ammonia solution (28 wt%) was added slowly to adjust pH value to 9. Then silica fiber was placed in precursor solution and aged at room temperature for 12 h. The formed solid was filtered and washed with DI water. The HT sample was synthesized with the same synthesis solution as for preparing the DPNH sample, and the hydrothermal preparation condition was temperature of 140 °C for 24 h in a Teflon-lined autoclave. All catalysts were dried at temperature of 120 °C for 12 h and calcined at temperature of 400 °C for 3 h under static air.

2.2. Catalyst characterization

The overall morphologies and diameters of the electrospun fibers were determined with scanning electron micrographs obtained using a JEOL JSM-5410LV scanning electron microscope