Fuel 164 (2016) 347–351

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Short communication

Fe_2O_3 nanoparticles encapsulated in TiO_2 nanotubes for Fischer–Tropsch synthesis: The confinement effect of nanotubes on the catalytic performance

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HIGHLIGHTS

- A novel Fe-based confinement catalyst was prepared by vacuum-assisted impregnation.
- Catalyst with confinement effect shows an improved yield of oil phase product.
- Fe-in-TNT catalyst has a higher C_{5+} and C_{12+} hydrocarbons selectivity than Fe-out-TNT.
- Confinement effect of encapsulated Fe_2O_3 can enhance the reabsorption of α-olefin in FTS.

ARTICLE INFO

Article history:
Received 20 April 2015
Received in revised form 30 September 2015
Accepted 30 September 2015
Available online 22 October 2015

Keywords:
Confinement effect
TiO_2 nanotube
Fischer–Tropsch synthesis
Iron-based catalysts
Elongation of carbon chain

ABSTRACT

The catalysts with high activity and selectivity, especially the latter, play a key role in Fischer–Tropsch synthesis technology. Herein, a novel Fe-based confinement catalyst, Fe_2O_3 encapsulated in TiO_2 nanotubes, was prepared by a method of vacuum-assisted impregnation. The catalyst presented an excellent yield of oil phase hydrocarbons and C_{5+} selectivity due to the confinement effect. This interesting phenomenon was discussed from the view of the restrained molecular movement and enhanced readsorption of short-chain α-olefins in the confined space of TiO_2 nanotube channels. The results over this novel confinement catalyst revealed a promising research prospect on adjusting the product distribution to long-chain hydrocarbons for Fe-based Fischer–Tropsch catalyst.

1. Introduction

Fischer–Tropsch synthesis (FTS) is of great strategic significance for the energy shortage, because it can produce clean hydrocarbon fuels (e.g., gasoline, diesel, and aviation kerosene) and chemicals from syngas ($CO + H_2$) via the ways of coal indirect liquefaction and gas to liquid (GTL) technology [1–3]. The recent development of novel catalysts with high activity and selectivity, especially the latter, is the key to improve FTS technology and one of the main focuses in the academic community [4].

The typical FTS catalysts for practical industrial production are Co and Fe [5]. Cobalt catalysts have a higher activity and produce more long-chain hydrocarbons. To increase the selectivity of product, Noritatsu Tsubaki prepared a core–shell catalyst with zeolite shell and Co/Al_2O_3 core for FTS and the long straight hydrocarbons (C_{12+}) can be cut into desired middle isoparaffins [6]. However, cobalt catalysts are expensive and sensitive to reaction conditions. Iron is much cheaper and suitable for reaction of practical syngas with low H_2/CO ratios such as those obtained from biomass or coal [4]. Iron-based catalysts are usually used to produce olefins and short-chain molecules [7]. It could be meaningful to produce more specified long-chain hydrocarbons by adjusting iron-based catalyst structure. The selectivity could be effectively controlled by adjusting the structure of catalyst, such as the particle size of Fe and pore structure of support [8,9]. Recently, a prominent work involved with confinement effect of Carbon Nanotubes (CNTs) reported by Bao's group should be noted [10,11]. They have encapsulated

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http://dx.doi.org/10.1016/j.fuel.2015.09.089
0016-2361/

Fe_2O_3 nanoparticles into the inner surface of CNTs. It's found that the confinement effect could improve catalytic activity greatly and, prominently the space–time yield and selectivity for C_{5+} hydrocarbons. In our previous work, we have fabricated novel confinement catalysts with metal (Pt [12] and Pd [13]) or sulfide (CdS [14]) nanoparticles entrapped in TiO_2 nanotubes (TNTs), and proved that the confinement of TNT could modulate the catalytic performance either. To the best of our knowledge, there's no report about the preparation and confinement effect of TiO_2 nanotube on the entrapped Fe_2O_3 for FTS. Herein, a novel Fe-based confinement catalyst, Fe_2O_3 encapsulated in TiO_2 nanotubes, was prepared by a method of vacuum-assisted impregnation and the FTS performance was investigated.

2. Experiments

2.1. The preparation of catalysts

The titanate nanotubes (TNT) were prepared via a promoted hydrothermal method as presented in supplementary information. The fresh TNTs powder was added into a cetyltrimethylammonium bromide (CTAB) aqueous solution and kept stirring. Then tetraethoxysilane (TEOS) ethanol solution was added into the mixture. After stirring for 1.5 h, an $NH_3 \cdot H_2O$ solution was added dropwise slowly and kept stirring for 2 h. The obtained white precipitate was then washed with ethanol for several times to remove additional CTAB and dried at 343 K. Finally, the sample was calcined at 873 K for 2 h to get the modified TNT.

The Fe-in-TNT catalyst with Fe_2O_3 nanoparticles inside the nanotube channels was prepared by vacuum assisted-impregnation method. The modified TNT was impregnated with $Fe(NO_3)_3$ aqueous solution under a vacuum atmosphere ($p < 0.01$ Pa) to strengthen the capillary effect that drives the precursor solution into the inner pore of TNT [15]. The impregnation was conducted for 2 h, and dried at 343 K for 12 h followed by calcination at 673 K in a flow of N_2 for 2 h. The Fe loading amount of Fe-in-TNT is 15% if not mentioned in this paper. A reference catalyst of Fe-out-TNT, with Fe_2O_3 nanoparticles outside the TNT surface, was also prepared using a conventional impregnation method but without the vacuum assisted solution.

2.2. The characterization of catalyst

X-ray diffraction, N_2 adsorption–desorption, Transmission electron microscopy, X-ray photoelectron spectroscopy and Hydrogen temperature-programmed reduction are listed in supplementary information.

2.3. FTS reaction performed on the prepared catalysts

The catalytic performance of Fe-in-TNT and Fe-out-TNT catalysts towards FTS was investigated with a stainless steel fixed-bed microreactor. 1.0 g of catalyst was packed inside. First the reactor temperature was increased to 673 K and held for 12 h in a syngas atmosphere (0.1 MPa, $H_2/CO/N_2$:47.5/47.5/5 mol%) for the activation. Then the reactor temperature was reduced to 553 K, the pressure of syngas was gradually increased to 2 MPa and at a flow rate of 50 mL min^{-1} for the FTS reaction.

3. Results and discussion

The TEM images of catalysts are shown in Fig. 1. Since Fe_2O_3 and TiO_2 have similar TEM contrast, the images of TiO_2 nanotubes and iron particles can be hardly distinguished. In the case of Fe-in-TNT, most particles are deposited on the inner surface of nanotubes as indicated by Fig. 1a and b, suggesting that the vacuum-assisted impregnation method could facilitate entrapment of Fe^{3+} ions into the TNT channels. It can be seen that the entrapped particles are flat ellipses with length of 3–8 nm rather than conventional spheres because of the narrow inner space and small contact angle of precursor solution with hydrophilic nanotubes wall. For the Fe-out-TNT, most dark spots in the size range of 4–8 nm are randomly dispersed on the outside surface of TNT, as shown in Fig. 1c and 1d. And the fringe spacing value (~2.46 Å) of the particles in Fig. 1d corresponds to the (1 1 0) lattice spacing of hematite [16].

Pore distributions obtained from the nitrogen adsorption–desorption isotherms for catalysts are shown in Fig. 2. Textural properties calculated by the Brunauer–Emmet–Teller (BET) method are listed in Table 1. Both samples have similar surface area which is close to that of TiO_2 nanotubes. Besides the close pore size of about 9 nm (peak B1 and B2), Fe-in-TNT has an additional pore size of about 2.4 nm as shown at peak A. Peak B1 and B2 should be the pore of TNT nanotubes, and the additional peak A for Fe-in-TNT can be attributed to the fact that Fe_2O_3 particles encapsulated inside TNT narrow the inner space. The BET data further indicate that in the case of Fe-in-TNT prepared by vacuum-assisted impregnation method, most of Fe_2O_3 particles are encapsulated inside the nanotube channels; while in the case of Fe-out-TNT with conventional impregnation method, there are more particles supported on the outside nanotube walls.

The reducibility of catalysts is evaluated by H_2-TPR, as shown in Fig. 3. Two prominent peaks can be identified on the patterns of catalysts. The low temperature reduction peak can be assigned to the reduction of Fe_2O_3 to FeO [17,18]. The wide high temperature peak can be associated with the reduction of FeO to metallic Fe. It should be noted that, both the reduction peaks in the Fe-in-TNT shifted to lower temperature compared with the Fe-out-TNT, indicating the improved reducibility properties of Fe-in-TNT. This result suggests that the Fe_2O_3 nanoparticles encapsulated in the TNT are easier to be reduced. Similar finding has been reported on the Fe particles confined in CNTs, which was attributed to the confinement effect of CNTs on the entrapped Fe [10].

Table 2 shows the catalytic activity of the Fe-in-TNT and Fe-out-TNT catalysts under the reaction temperature of 573 K. The CO conversion is 71% and 35% over Fe-out-TNT and Fe-in-TNT, respectively, indicating that Fe-in-TNT is less active for FTS than Fe-out-TNT. This may be due to the fact that the narrow confinement space of Fe-in-TNT restrains the diffusion of reactants and decreases the gas flow rate, reducing CO conversion during FTS. On the other hand, the amounts of iron species inside the TNT support is few possibly than that outside the TNT support, resulting in less available active Fe sites provided by Fe-in-TNT. The yield of liquid product of Fe-in-TNT is 568 gC_{5+}/kg_{cat} h, which is about twice as much as that of the comparison catalyst (273 gC_{5+}/kg_{cat} h). This shows improved activity in long-chain product of confinement catalyst.

The product selectivity of two catalysts is presented in Table 2. The CH_4 selectivity over Fe-in-TNT is 15%, which is much lower than 32% over Fe-out-TNT. The selectivity of C_2–C_4 short-chain hydrocarbons over Fe-in-TNT is about half of that over Fe-out-TNT. Remarkably, Fe-in-TNT has higher selectivity of C_{5+} longer-chain hydrocarbons, especially for the part of C_{12+}, which can reach 32%.

Fig. 4 shows the detailed product distribution of liquid hydrocarbon products (C_{5+}) for two samples. Fe-out-TNT catalyst exhibits a very narrow product distribution (mainly C_6–C_{12}) and few C_{12+} hydrocarbons, as the selectivity is only 2%. In contrast, Fe-in-TNT has a wider product distribution and the peak moves towards high carbon number (C_9–C_{10}). Meantime, much more C_{12+} hydrocarbons (32%) are formed.