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Preparation of a novel structured catalyst based on aligned carbon nanotube arrays for a microchannel Fischer-Tropsch synthesis reactor

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Abstract

A novel microstructured catalyst based on aligned multiwall carbon nanotube arrays was synthesized and tested for Fischer-Tropsch synthesis (FTS) reaction in a microchannel reactor. Fabrication of such a structured catalyst first involved metal organic chemical vapor deposition (MOCVD) of a dense Al_2O_3 thin film over FeCrAlY foam to enhance the adhesion between ceramic-based catalyst and metal substrate. Aligned multiwall carbon nanotubes were deposited uniformly over the substrate by controlled catalytic decomposition of ethylene. These nanotube bundles were directly attached to FeCrAlY foam through a submicron layer of oxide thin film. Coating the outer surfaces of these nanobundles with an active catalyst layer forms a unique hierarchical structure with fine interstitials between the carbon nanotube bundles. The microstuctural catalyst possessed superior thermal conductivity inherent from carbon nanotube, which allows efficient heat removal from catalytic active sites during exothermic FTS reaction. The concept was tested and demonstrated in a microchannel fixed bed FTS reactor. FTS turn-over activity was found to enhance by a factor of four owing to potential improvement in mass transfer in the unique microstructure. Furthermore, improved temperature control with the carbon nanotube arrays also allows the Fischer-Tropsch synthesis being operated at temperatures as high as 265 °C without reaction runaway.

Keywords: Fischer-Tropsch synthesis; Carbon nanotube; Engineered catalyst; Microchannel reactor

1. Introduction

Recently, Fischer-Tropsch synthesis (FTS) has received increasing attention due to its promising potential as a cost effective route to produce clean transportation fuel from natural gas. Commercial FTS processes to date are based on tubular fixed bed, circulating fluidized bed, or slurry reactors configurations loaded with supported cobalt or iron catalysts. Advantages and downsides of each reactor type have been well investigated in the last 60 years' industrial practice [1–5]. In FTS reactor where gas–liquid–solid phases present simultaneously, the reactor is likely operated under significant heat and mass transfer resistances, regardless of the reactor configurations. For example, commercial slurry based FTS reactor has the advantage of fast heat removal to minimize local hot spots. However, inherent mass transfer resistances encountered from the three phases reaction system and the difficulty in catalyst filtration are generally unavoidable. To obtain a high yield and selectivity to heavy hydrocarbons, all commercial FTS processes are operated at relatively low temperatures and space velocities to avoid thermal runaway. In other words, catalytic active sites has not been fully utilized without radical improvement in mass and heat transfer in reactor and catalyst configurations.

Recent advancement in microchannel chemical reactors technology has opened up new opportunities for chemical process intensification. Microchannel chemical reactors, with its characteristics of unprecedented temperature control and improved mass transfer [6–10] provides a promising route to FTS process intensification. We have recently developed engineered catalysts based on porous substrates with enhanced heat and mass transfer while maintaining a low pressure drop for use in microchannel chemical conversion reactors [11]. One of the porous substrates is metal foam, an open cell sintered porous structure made from a metal or alloy material. Commercially available metal foams are made from, but not limited to, Ni, stainless steel, FeCrAlY alloy or Cu. Unlike

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conventional monolith with straight channels, metal foams are formed with three dimensional interconnected void spaces with a uniform pore diameter ranged from 10 to 5 mm and a void fraction of 80–97%. These open interconnected structures provide excellent mixing while maintaining a low pressure drop across the bed. In addition to these properties, high thermal conductivity and ease of metallurgically bonded to metallic surfaces have rendered their use in compact heat exchanger [12] and fuel cell system. For the same reason, microchannel chemical reactor system utilizes metal foam as structured support with catalytically active sites anchored to the foam surface. Recent works in microchannel reactor fabrication area reported the use of intermetallic FeCrAlY alloy in the forms of felt [13] or foam [14] as catalyst structured support. Surfaces of FeCrAlY, upon high temperature oxidation, formed a dense layer of native aluminum oxide scale that promotes adhesion of supported oxide catalyst without degradation.

Typical preparation of metal foam catalyst involves washcoating a catalyst slurry directly over the native aluminum oxide scale formed after high temperature treatment. However, poor adhesion of ceramic-based catalyst powder over metal surface often leads to peeling and eventually structured degradation. Recently, we have demonstrated a technique to enhance the adhesion by metal organic chemical vapor deposition (MOCVD) of an interfacial oxide between the FeCrAlY felt and the catalyst layer [11]. It is recognized that catalyst adhesion depends not only on the substrate surface but also on the overall coating thickness. Catalyst site density can be increased by simply increasing the amount of catalyst coated on the metal foam surfaces, which, unfortunately, leads to more cracking and peeling of the coated layer or increased external mass transfer resistance during operation.

To increase catalyst site density without compromising its mass transfer characteristic and potential degradation of the coating layer, we have investigated a novel method to fabricate an engineered catalyst based on the growth of aligned multi-wall carbon nanotubes over FeCrAlY foam substrate for use in a microchannel FTS reactor. Since the discovery of carbon nanotube over a decade ago, this novel class of material is known to offer unique physical and chemical properties. Specifically, we exploited its high thermal conductivity and high surface area when used as the catalyst substrate for microchannel reactor. In particular, we anchored catalytic actives sites over the outer surfaces of well aligned carbon nanotube bundles grown over FeCrAlY foam substrate. The resulting multilayer engineered catalyst structure was tested for FTS reaction in a microchannel reactor. Improvement of FTS reaction turn-over was demonstrated when compared with an engineered catalyst reference, synthesizing using the same method except without the carbon nanotube deposition step. High thermal conductivity of carbon nanotube coupled with active heat removal in a microchannel reactor [15–17] allow the FTS reaction proceeding at relatively high temperatures without loss in selectivity, leading to high space-time yield.

2. Experimental

2.1. Synthesis and fabrication of carbon nanotube engineered catalyst

A bimetallic Co–Re carbon nanotube based FTS engineered catalyst was fabricated through a series of sequential deposition using combined chemical vapor deposition and coating techniques as described below.

FeCrAlY (Porvair, Hendersonville, N.C.) intermetallic alloy foam with 80 ppi pore was cut to 3.56 cm × 0.90 cm × 0.15 cm. The sample was loaded in a 1inch OD tubular quartz reactor, oxidized in 100 sccm flowing air at 900 °C for 2 h under a reactor pressure controlled at 20 Torr. Under these conditions, surface of FeCrAlY undergoes oxidation to form a native aluminum oxide layer.

Following the surface oxidation, a dense and pinhole-free interfacial aluminum oxide layer was deposited over the native oxide layer by metal-organic chemical vapor deposition (MOCVD) at 900 °C in the tubular reactor using aluminum isopropoxide as the precursor. During the MOCVD process, 30 sccm of N_2 was flowed continuously through a bubbler that contained aluminum isopropoxide precursor and maintained isothermally at 110 °C. The N_2 stream was saturated with aluminum isopropoxide precursor and was then introduced along with 30 sccm of air and another 100 sccm of makeup N_2 over the foam substrates at a chamber pressure of 5 Torr over a 1 h growth period. Under these conditions, the growth rate of aluminum oxide thin film was found to be approximately 0.3 μm/h.

Following the MOCVD step, the alumina coated FeCrAlY substrate was cooled to room temperature and dip coated in a precursor sol of Fe/mesoporous silica. To make the precursor sol, tetraethylorthosilicate (TEOS), polyoxyethylene 10 cetyl ether ($C_{16}EO_{10}$), water, ethanol, and small amount of hydrochloric acid (HCl) was dissolved in a glass vial at molar ratios of $5H_2O{:}10C_2H_5OH{:}0.1\ C_{16}EO_{10}{:}1.0\ TEOS{:}0.01\ HCl$. The solution was stirred at 30 °C with a magnetic stir bar for 1 h before mixing with a 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$ solution at a volume ratio of 1:1. The precursor sol was then stirred for another hour prior to the dipcoat onto metal foam surface.

FeCrAlY metal foam substrate was dip coated with the solution, followed by rapid drying. The coated foam was then calcined at 450 °C for 2 h in air to yield a 1–2 μm thin layer film of supported Fe oxide nanoparticles over mesoporous SiO_2. This layer serves as the seeding layer for carbon nanotube growth.

Growth of carbon nanotubes was carried out by catalytic decomposition of ethylene in a 1inch OD tubular quartz reactor at 1 atmosphere. In a typical run, the coated substrate was heated under 500 sccm of N_2 to 700 °C. Pure ethylene gas (99.9%) was then introduced into the reactor at a flow rate of 500 sccm for 5 min. The reactor was cooled down slowly to 450 °C, introducing air for 5 min at 450 °C before further cooling to room temperature under flowing N_2.

Bimetallic Co–Re/Al_2O_3 catalyst was deposited onto the substrate by sequential dip-coating of alumina sol (PQ corporation) and an aqueous Co–Re precursor solution. The alumina sol was prepared from commercial sol (PQ corporation) diluted with ethanol (1:3 volume based). The Co–Re precursor solution consisted of 3.74 mol/L of dissolved cobalt nitrate. Perrhenic acid was added in the solution to give a Co/Re ratio of 29.8.

Final calcinations and intercalcination between coatings was carried out in air at 350 °C for 3 h. Upon completion of synthesis and fabrication, a microstructured catalyst consists of carbon nanotube arrays and a metal oxide layer over the FeCrAlY foam, as depicted in a cartoon shown in Fig. 1. Separately, a structured engineered catalyst of metal foam/Al_2O_3/Co–Re–Al_2O_3 without the carbon nanotube arrays was fabricated for comparison purposes. This baseline sample was fabricated following the same procedure described above, except that the step of carbon nanotube growth was omitted from the preparation.

2.2. SEM characterization

High resolution SEM micrographs were obtained over a LEO Gemini 982 digital field emission gun scanning electron microscope (FEG-SEM). The micrographs were collected at a working distance of 8 mm using a scintillator-type secondary electron detector, which was integrated above the objective lens of the microscope. Samples were mounted on carbon tape.

2.3. Catalyst activity testing and products measurements

The experiments were carried out in a microchannel reactor made of 316 stainless steel, with a channel dimension of 3.56 cm × 0.90 cm × 0.15 cm. The metal foams used for preparing structured engineered catalysts were machined to match the internal geometry of the reactor channel, where bypass between the structured catalyst and the channel wall was minimized. Engineered catalyst was prepared as described in the previous section and inserted into the reactor channel.

Prior to F-T reaction, catalysts were reduced under a flowing 5% H_2/Helium mixture at 350 °C for 12 h. After reduction was completed, reactor was cooled down to the reaction temperature (e.g., 240 °C), followed by pressurizing the reactor with the reduction gas to 1 5 MP before switching to syngas at a H_2/CO ratio of 2:1. The typical feed composition was $CO:H_2:Ar = 32:64:4$. Ar gas in the feed served as an internal standard for CO conversion and product selectivity calculation purposes. Total feed flow rate was set to achieve a desired gas hourly space velocity (GHSV) of 14,400 h^{-1}. The stream leaving the reactor (unreacted syngas and hydrocarbon products) was separated into condensed and non-condensable products. A pressurized cold trap operated at 0 °C was installed to capture majority of condensable products (C_4 and above). Gaseous products were analyzed by gas chromatography to obtain CO conversion and product selectivity. Carbon monoxide conversion and product selectivity were calculated based on feed and product flow rates and carbon balance.

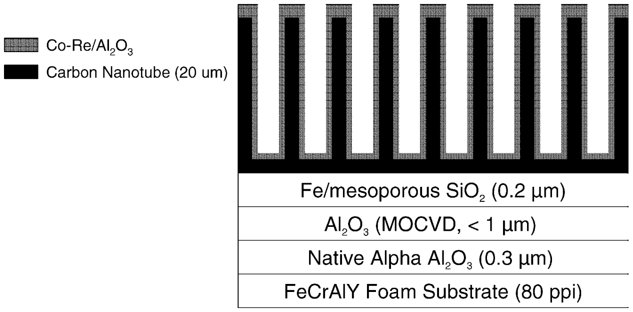

Fig. 1. Schematic of engineered catalyst based on multilayer carbon nanotube arrays for Fischer-Tropsch synthesis in a microchannel reactor.

3. Results and discussion

3.1. Physical morphology of the CNT modified FeCrAlY substrate

Fig. 2a shows the microstructure of a 80 ppi FeCrAlY foam under SEM at a magnification of 100×. The foam consists of continuous interconnected open voids with pore size ranging from 180–220 μm. Rapid oxidation in air at 900 °C for 2 h facilitates the growth of a well adherent native alpha aluminum oxide thin film on the surface as a result of an outward diffusion of Al from the alloy matrix and an inward diffusion of gaseous O_2. This native Al_2O_3 film serves as the nucleation layer for the subsequent metal-organic chemical vapor deposition (MOCVD) of Al_2O_3. Fig. 2b and c depicts the metal-ceramic interface after the MOCVD growth. As shown in the figures, a uniform layer of highly dense alpha alumina thin film with a thickness of approximately 0.28 μm was deposited over the FeCrAlY surface. Under SEM, it is unlikely to differentiate the native Al_2O_3 from the MOCVD grown Al_2O_3 layer, which is most likely due to good interatomic mixing between the two layers. It is worth noting that having an additional MOCVD Al_2O_3 layer not only increases the adhesion between the metal foam substrate and the Fe/mesoporous SiO_2 layer, but also protects the FeCrAlY from corrosion during carbon nanotube growth at high temperatures.

Multiwall carbon nanotube (CNT) array is deposited over the metal foam to further enhance the surface area available for catalyst coating. First, a submicron layer of mesoporous Fe/SiO_2 thin film is coated on the foam from a surfactant templating sol precursor. This layer serves as a seeding layer for CNT growth. Compare to conventional wash coating from suspended powder slurry, dip coating the metal foam with a sol gel precursor has many advantages. The current approach used direct gelation method, where the sol solution gelled and dried onto the metal foam. During the drying and gelation process, the mesoporous material adheres strongly onto the metal foam substrate, thus maintaining an intimate contact without formation of voids or micropores in the interface which would increase the heat transfer resistance of the final engineered catalyst under operation.

A layer of multiwall carbon nanotube arrays is grown over the Fe/SiO_2 coated foam by catalytic decomposition of ethylene at 700 °C. Fig. 3a–d show representative SEM micrographs of carbon nanotube (CNT) modified FeCrAlY foam under various

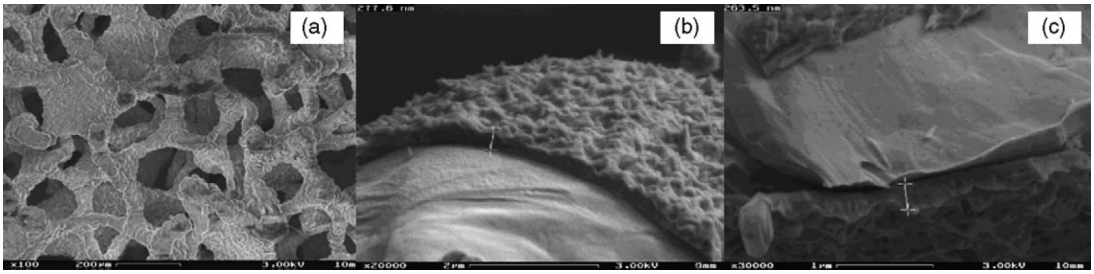

Fig. 2. Scanning electron micrographs of a bare FeCrAlY foam (a) and interface of the native and MOCVD grown Al_2O_3 thin film over FeCrAlY foam (b and c).

magnifications. Compared to a bare FeCrAlY foam (Fig. 2a), the nanotube modified FeCrAlY foam retained its open void structure (Fig. 3a and b) while additional interstitials are created between the nanotube bundles. Fig. 3b shows SEM image of an open cell in the FeCrAlY foam coated with carbon nanotubes. The carbon nanotube arrays provide an additional layer of ‘‘carpet’’ like surface covering the bare FeCrAlY foam. Further magnification, as illustrated in Fig. 3c, shows carbon nanotube layer in a thickness of 35 μm deposited after a growth period of 10 min. The growth rate and thickness of the carbon nanotube layer can be controlled by varying the deposition time. High magnification SEM in Fig. 3d shows bundle of aligned multiwall carbon nanotube strands with individual diameter in the range of 50–80 nm. Compared to a bare FeCrAlY foam, this additional ‘‘carpet’’ like layer of high-density carbon nanotubes significantly enhanced the available

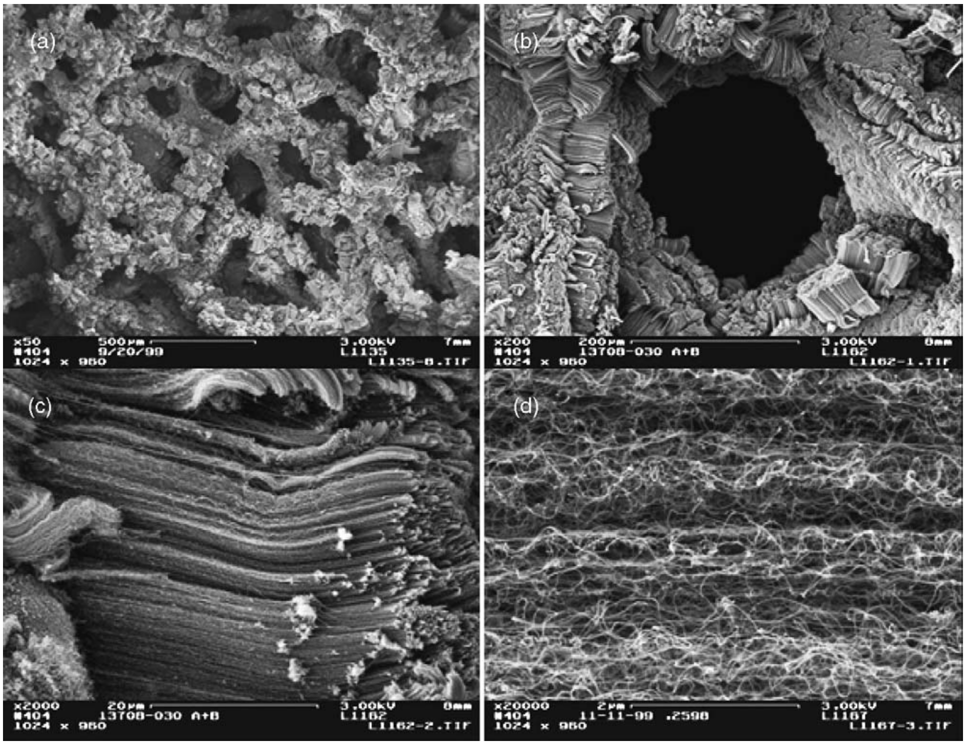

Fig. 3. Microstructure of carbon nanotubes grown on FeCrAlY foam structures under SEM at various magnifications: (a) 50×; (b) 200×; (c) 2000× and (d) 20000×.

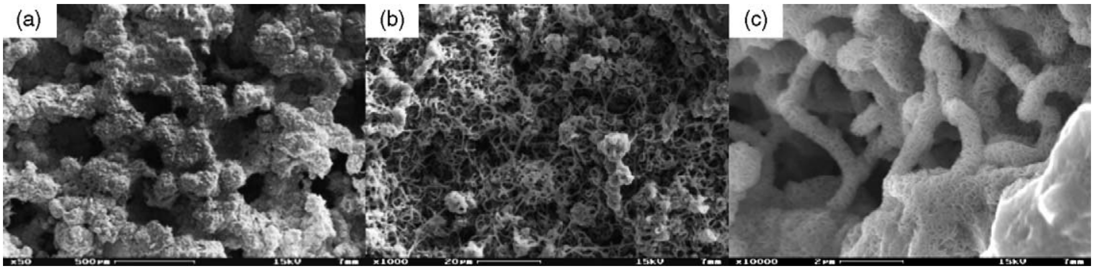

Fig. 4. Carbon nanotubes grown on FeCrAlY foam structures with Al_2O_3 coating under SEM at various magnifications: (a) 50×; (b) 1000× and (c) 10000×.

Table 1
Fischer-Tropsch synthesis activity over carbon nanotube structural engineered catalyst

Structural foam support	Temp (°C)	Weight of Co–Re/ Al_2O_3 (g)	Concentration of Co–Re (wt.%)	CO Conv.	CH_4 selectivity	Specific activity (mmol CO conv/g Co/h)
Carbon nanotube /FeCrAlY	266	0.0493	37% Co–4% Re	42%	27%	2362
FeCrAlY (baseline)	265	0.0662	50% Co–5% Re	20%	31%	645

surface area for anchoring catalyst particles. For example, the bare FeCrAlY has a specific surface area that is less than 0.5 m^2/g. When coating a 35 μm carbon nanotube layer onto the engineered catalyst with dimensions described above, the BET surface area per unit pieces of the engineered catalyst is estimated to increase by a factor of 10. The carbon nanotube arrays not only provide larger surface area for anchoring catalytic active sites, but also provide larger interstitials (>50 nm) that enhances mass transfer. Following the nanotube growth, a layer of high surface area gamma Al_2O_3 is wash coated over the outer surface of these nanotube bundles. Fig. 4a–c shows the microstructure of an engineered catalyst with the Al_2O_3 coating over the carbon nanotubes. With a proper control of Al_2O_3 concentration in the precursor sol and its rheological properties, the resulting engineered catalyst retained its open void structure and fine interstitials within the carbon nanotube bundles. As shown in Fig. 4, interstitials within the cabon nanotube bundles were retained without over coating with excess Al_2O_3 particles. Bimetallic Co–Re particles are anchored over the outermost layer gamma Al_2O_3 by sequential dip coating in an aqueous precursor solution, as described in the experimental section.

The resulted microstructured catalyst allows passage of gas and liquid at high flow rates without significant pressure drop. More importantly, the carbon nanotube based layer, with its high thermal conductivity, is expected to promote active heat removal from catalytic active sites. This concept is demonstrated using FTS reaction as an example.

3.2. Performance of structured catalysts based on carbon nanotube arrays in F-T synthesis

Table 1 shows the FTS performance of the carbon nanotube engineered catalyst. For comparison purposes, a baseline catalyst was synthesized following the same procedure, except that the CNT growth was omitted from the synthesis steps. The performance of a baseline engineered catalyst is included in the table for comparison. Specific activity data were derived from steady state conversion at a time-on-stream (TOS) greater than 96 h.

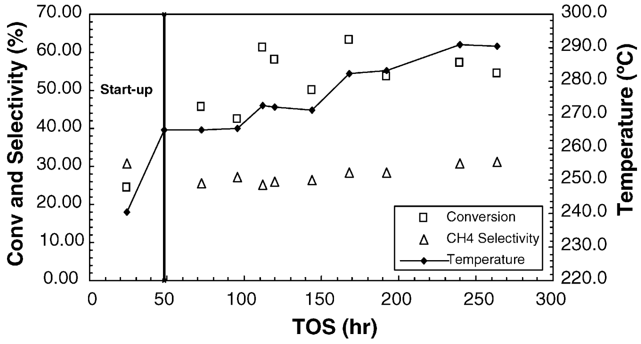

Fig. 5. Performance of CNT modified structured FTS engineered catalyst (active component: Co–Re/Al_2O_3, GHSV = 14,400 h^{-1}, P = 1.5 MPa).

As shown in Table 1, the CNT structured catalyst exhibited a higher CO conversion and a lower methane selectivity. In addition, the specific activity was enhanced by approximately a factor of 4. This could most likely be due to improvements in both mass and heat transfer properties of the microstructure catalyst.

Heat generated during FTS reaction can be conducted along the length of carbon tube then quickly dispatched from active sites, lowering the methane selectivity. Fig. 5 shows the time-on-stream conversion and selectivity of the CNT structured catalyst under increasing bed temperature. It is demonstrated that the CH_4 selectivity remained stable to a bed temperature as high as 290 °C. We have previously performed FTS reaction under similar conditions over a powdered Co–Re/Al_2O_3 catalyst (60–100 mesh) packed in the same microchannel reactor without supporting the catalyst over an engineered structure. In this configuration, we have found that the FTS reaction is unlikely to carry out at an average catalyst bed temperature exceeding 240 °C while maintaining a reasonable CH_4 selectivity. Above this temperature, methanation reaction dominates.

4. Conclusion

We have developed and fabricated a novel engineered catalyst based on multilayer thin film of Al_2O_3 and carbon nanotube arrays over FeCrAlY metal foam. The fabrication of such a novel and structured catalyst involved combined methods of MOCVD, catalytic nanotube growth, and dip-coating of active catalyst components. When integrated into a microchannel reactor, this microstructured engineered catalyst exhibited a factor of four enhancement in Fischer-Tropsch synthesis activity compared to an engineered catalyst structure without the carbon nanotube arrays. This is most likely due to improve mass and heat transfer which has also allowed the Fischer-Tropsch synthesis being operated at higher temperatures without selectivity runaway favoring methane formation.

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