Iron catalyst encapsulated in carbon nanotubes for CO hydrogenation to light olefins

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ABSTRACT

Fe-based catalyst is an outstanding candidate for the Fischer-Tropsch reaction to get light olefins from syngas directly. However, exposed Fe species are susceptible to sintering and coking, which lead to deactivation. Here, we demonstrate that Fe nanoparticles encapsulated in pod-like carbon nanotubes (Pod-Fe) can be used as an efficient Fischer-Tropsch catalyst to produce light olefins. It gave a higher selectivity of light olefins (45%) and high stability over 120 h reaction (P = 0.5 MPa, T = 320 °C, CO:H₂ = 1:2, gas hourly space velocity = 3500 h⁻¹). A catalyst with exposed Fe particles on the outside of the Pod-Fe (FeOₓ/Pod-Fe) catalyst showed a selectivity of light olefins of 42%, but had a significantly lower stability due to the agglomeration of Fe nanoparticles and carbon deposition. These results indicated that the graphene shell of Pod-Fe played an important role in protecting the Fe particles and provided a rational way to enhance the activity and stability of Fe-based catalysts in high temperature reactions.

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1. Introduction

Fischer-Tropsch synthesis (FTS) has attracted wide attention in recent years for its potential application in converting coal, natural gas or biomass to useful hydrocarbons and other chemicals [1–4]. Compared to other FTS catalysts like Co, Ni and Ru, a Fe-based catalyst has higher feedstock flexibility [5–8]. Fe-based catalysts can be used in CO-rich syngas directly with almost no need for further H₂/CO ratio adjustment because of their high water gas shift activity. The tunable selectivity makes an Fe-based catalyst a promising catalyst for generating hydrocarbons with different chain lengths [9–13]. However, a Fe-based catalyst faces a big problem as coking and sintering can easily happen with Fe and lead to the deactivation of the catalyst [14–16]. To stabilize Fe particles from aggregation, different supports such as silica, alumina and zeolite are often used to disperse Fe particles [17–20]. But these oxide supports have a strong interaction with Fe, especially with highly dispersed Fe particles, and form iron aluminates [21] and iron silicates [22,23] which are hard to reduce and lead to low activity. On the other hand, when using weakly interactive supports like active carbon or carbon nanofibers, the weak physical binding between its surface and Fe nanoparticles does not protect Fe-based nanoparticles from aggregating and coking under reaction conditions [3].

To solve this, we recently proposed the concept of “chainmail for catalyst”, namely, encapsulating a transition metal catalyst (such as Fe, Co, Ni, and their alloys) in carbon shells [24–27]. The stable carbon shell protect the inner metal particles from oxidizing in air or etching by acid, while the penetration elec-
trons of the transition metals promote the catalytic reaction on the carbon surface [24,27,28]. This strategy can significantly enhance the activity and stability of non-precious metal catalyst under harsh conditions, as has been demonstrated by our group and other groups in the fields of the oxygen reduction reaction (ORR) in fuel cells [24,25,29,30], hydrogen evolution reaction (HER) [26,27], O2 reduction in dye-sensitized solar cells (DSSCs) [31], and catalytic oxidation and reduction reactions in heterogeneous catalysis [32,33]. Inspired by this, we report that Fe nanoparticles encapsulated in the compartment of bean pod-like carbon nanotubes (Pod-Fe) can be used as a highly stable catalyst for CO hydrogenation to light olefins at high temperature. It can efficiently avoid the agglomeration and coking of Fe nanoparticles during the reaction.

2. Experimental

2.1. Catalyst preparation

FeOx/Pod-Fe was synthesized by the method of our previous report [24]. Briefly, 3.0 g ferrocene (Tianjin Bodi Chemical Holding Co., Ltd.) and 3.0 g sodium azide (BDH Chemicals Ltd. Poole England) were put into a 40 mL stainless steel autoclave with a TCD, and a modified Al2O3 capillary column to analyze hydrocarbons was calculated on a carbon atom basis excluding CO2.

The Fischer-Tropsch reaction was carried out in fixed bed reactors with a quartz inner lining. The feed flow was a mixture of H2/CO/Ar (63.3/31.7/5, vol%) and Ar was used as an internal standard. Typically, 100 mg catalyst was used to react syngas under different gas hourly space velocities (GHSV) and temperatures. All gas lines after the reactor were kept at 140 °C. All products were analyzed by an online gas chromatography (Agilent 7890A) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Three chromatography columns were used, Porapak Q and 5 Å molecular sieves packed columns to analyze CO, CO2, CH4 and Ar with a TCD, and a modified Al2O3 capillary column to analyze C1–C8 range hydrocarbons with a FID. The selectivity of the hydrocarbons was calculated on a carbon atom basis excluding CO2.

2.2. Characterization

The Fe concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). FeOx/Pod-Fe was further treated by refluxing in 25 wt% HCl aqueous solution at 90 °C for 4 h, followed by the same washing and drying process as for FeOx/Pod-Fe. The resulting sample was denoted as Pod-Fe. The Fe content of Pod-Fe was 12.8% as measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

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2.3. Catalytic reaction

The morphology of Pod-Fe and FeOx/Pod-Fe is shown in Fig. 1(a) and 1(b). One can clearly see that the Fe nanoparticles of Pod-Fe were completely encapsulated in the CNTs with usually one or two Fe particles in one compartment, while the iron nanoparticles of FeOx/Pod-Fe were distributed both inside and outside the carbon nanotube. The XRD patterns showed that Pod-Fe contained only metallic iron, while FeOx/Pod-Fe showed both metallic iron and characteristic iron oxide peaks (Fig. 1(c)). X-ray photoelectron spectroscopy (XPS) in our previous work also showed that the Fe in Pod-Fe was metallic, while both Fe3+ and Fe0 were observed in FeOx/Pod-Fe [24]. The above results indicated that the exposed Fe particles on the...
outside of FeO$_x$/Pod-Fe were easily oxidized, while the Fe nanoparticles encapsulated in Pod-Fe were well protected by the graphene layer and remained in a metallic state.

We then evaluated the performance of the two catalysts in FTS. As the activity and selectivity of the FTS reaction are sensitive to the GHSV and reaction temperature, we investigated the reaction under different GHSVs and temperatures as shown in Tables 1 and 2 for Pod-Fe and FeO$_x$/Pod-Fe. With increased GHSV, the CO conversion of both catalyst decreased, which is consistent with the reported literature [7]. When the GHSV was higher than 3500 h$^{-1}$, both catalysts showed a selectivity towards light olefins of around 40%. At very low GHSV (lower than 500 h$^{-1}$), the selectivity towards light olefins slightly decreased.

The influence of the temperature for both samples are summarized in Fig. 2. Comparing the selectivity of Pod-Fe and FeO$_x$/Pod-Fe, one can find that although both catalysts showed

Table 1

<table>
<thead>
<tr>
<th>GHSV/h$^{-1}$</th>
<th>10000</th>
<th>3500</th>
<th>1000</th>
<th>500</th>
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</thead>
<tbody>
<tr>
<td>CO conversion/%</td>
<td>1.3</td>
<td>2.4</td>
<td>8.9</td>
<td>19.4</td>
</tr>
<tr>
<td>CO$_2$ selectivity/%</td>
<td>11.0</td>
<td>14.3</td>
<td>22.6</td>
<td>30.3</td>
</tr>
<tr>
<td>CH distribution/%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>31.6</td>
<td>32.3</td>
<td>29.8</td>
<td>28.1</td>
</tr>
<tr>
<td>C$_2$–C$_4$</td>
<td>12.3</td>
<td>13.1</td>
<td>18.5</td>
<td>22.8</td>
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<tr>
<td>C$_5$–C$_7$</td>
<td>38.9</td>
<td>39.4</td>
<td>35.3</td>
<td>32.5</td>
</tr>
<tr>
<td>C$_5$+</td>
<td>17.2</td>
<td>15.2</td>
<td>16.4</td>
<td>16.6</td>
</tr>
<tr>
<td>C$_2$–C$_4$/C$_5$–C$_7$</td>
<td>3.2</td>
<td>3.0</td>
<td>1.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Reaction conditions: $P = 0.5$ MPa, $T = 320 ^\circ$C, CO:H$_2$ = 1:2.

Table 2

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>GHSV/h$^{-1}$</th>
<th>CO conversion (%)</th>
<th>CO$_2$ selectivity (%)</th>
<th>CH distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH$_4$</td>
</tr>
<tr>
<td>300</td>
<td>15000</td>
<td>4.0</td>
<td>46.8</td>
<td>18.7</td>
</tr>
<tr>
<td>300</td>
<td>10000</td>
<td>8.5</td>
<td>49.0</td>
<td>18.6</td>
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<td>3500</td>
<td>26.8</td>
<td>56.0</td>
<td>20.6</td>
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<td>15000</td>
<td>3.4</td>
<td>48.1</td>
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<tr>
<td>320</td>
<td>3500</td>
<td>20.7</td>
<td>51.9</td>
<td>26.2</td>
</tr>
</tbody>
</table>

Reaction conditions: $P = 0.5$ MPa, CO:H$_2$ = 1:2.
similar selectivities towards light olefins at different temperatures, the distributions of products were quite different. Pod-Fe showed much higher methane selectivity (30.6%) and lower C5+ selectivity (18.6%) at 300 °C (Fig. 2(a)). With increasing temperature up to 380 °C, the methane selectivity was 47.8% while the C5+ selectivity dropped to 6.3%. In contrast, FeO/x/Pod-Fe showed a lower methane selectivity (20.6%) and higher C5+ selectivity (31.4%) at 300 °C (Fig. 2b). These results indicated that the Pod-Fe catalyst could limit carbon chain growth as compared to FeO/x/Pod-Fe. Note that there was also an obvious difference of selectivity towards CO2 over the two catalysts. During FTS, the production of H2O is unavoidable. This is because FeOx particles on FeO/x/Pod-Fe promoted the water gas shift reaction leading to a higher CO2 selectivity since Fe3O4 is an active phase in the water gas shift reaction [34–36].

More importantly, the CO conversion of the catalysts was quite different with increasing temperature. Although the Pod-Fe sample showed a lower CO conversion than FeO/x/Pod-Fe due to the lower Fe content in Pod-Fe, the conversion increased with increasing temperature (Fig. 2(a)). Surprisingly, it still worked even at 380 °C without any deactivation. In contrast, the CO conversion of FeO/x/Pod-Fe steadily increased from 0.7% at 240 °C up to 26.8% at 300 °C (Fig. 2(b)). However, with further increasing temperature, the CO conversion dropped to 6.9% at 340 °C. It showed poor stability at higher temperature. These results demonstrated that the Pod-Fe catalyst significantly enhanced the catalytic stability compared to FeO/x/Pod-Fe.

To find the reason for the deactivation of FeO/x/Pod-Fe at high temperature, we carried out TEM characterization on both samples. The TEM images of Pod-Fe catalyst (Figs. 3(a) and 3(b)) showed that it still kept the morphology of the pod-like structure even after reaction at 380 °C for 10 h. No obvious agglomerated iron and carbon filaments were observed. However, for FeO/x/Pod-Fe after 10 h reaction at 340 °C (Figs. 3(c) and 3(d)), the tube morphology of the FeO/x/Pod-Fe was hardly observed. The Fe particles of the sample were agglomerated and the tubular structure was covered by carbon filaments and flakes, which would be the reason for the decrease of the catalytic activity. This confirmed that the carbon shells could protect the encapsulated Fe particles and maintain stability at high temperature.

We then further performed the stability test of both catalysts at a constant reaction temperature. As shown in Fig. 2, both Pod-Fe and FeO/x/Pod-Fe have good activity and selectivity at 320 °C, 0.5 MPa, GHSV = 3500 h⁻¹, so the stability test was carried out at this reaction condition. For Pod-Fe, as shown in Fig. 4(a), the CO conversion increased in the first 6 h, from 0.8% up to 4.2%, up to about 5 times. Then the CO conversion dropped a bit and kept stable in the next 120 h. The variation of selectivity towards light olefins was the opposite to the CO conversion. It decreased in the first 6 h and then increased and kept around 45%. It was quite different for FeO/x/Pod-Fe and the CO conversion dropped more than 50% in first 6 h, i.e., from 16.9% to 7.9% and then was constant afterwards (Fig. 4(b)). Meanwhile the selectivity towards light olefins kept around 42% as the reaction time increased, which was a little lower than the selectivity of Pod-Fe. These results further con-

![Fig. 3.](image)

![Fig. 4.](image)
firmed that Pod-Fe had a better catalytic stability compared to FeO/Fe-Pod.

In order to get a better understanding of the different behavior and active phase of the two catalysts, XRD patterns were used to examine the crystal structure of the used catalysts. As shown in Fig. 5, the main phase of Pod-Fe remained metallic. Only trace amount of iron carbide species can be observed. For FeO/Fe-Pod, there were mainly two kinds of iron carbides, namely, Hägg carbide (Fe₅C₂) and Cohenite (Fe₃C) after reaction. Both iron carbides were claimed to be active for FTS in the literature [14, 37]. It can be concluded that the iron oxide outside FeO/Fe-Pod will convert into iron carbides, which is easily formed for exposed iron under the FTS reaction condition [14, 16, 38].

The different performance of the two catalysts mainly originated from the deactivation of the Fe particles outside the carbon nanotube. FeO/Fe-Pod showed a higher activity at the beginning due to the higher Fe content and a large number of bare Fe particles outside the tube that formed iron carbide under the FTS reaction condition. But without the protection of the carbon shell, the activity of the Fe particles outside the CNTs dropped quickly due to carbon deposition and Fe agglomeration. In contrast, Fe particles encapsulated in the CNTs were efficiently prevented from structure damage and showed a high catalytic stability. According to our previous work, there is a strong interaction between encapsulated non-precious metals and the carbon shell, which lead to electron transfer from Fe to the carbon shell and reduced the local work function of the carbon surface where the Fe particles were located [24]. Molecules such as O₂, H₂O, I₃⁻, etc. can be adsorbed on the carbon shell surface of these catalysts and be activated [24, 26, 27, 31]. In this system, similarly, the penetrated electron from the Fe to the outside carbon surface probably promoted the adsorption of CO and H₂, and their subsequent activation since the Fe was encapsulated inside the compartment of the pod-like carbon nanotubes and cannot directly contact the reaction molecules. Meanwhile, the stable carbon shells efficiently protected the inner Fe from agglomeration. It should be noted that FTS reaction is very complex and the reaction mechanism on these catalysts still needs further study.

4. Conclusions

Pod-like carbon nanotubes with encapsulated Fe nanoparticles can be used as an efficient Fischer-Tropsch catalyst. The Pod-Fe catalyst showed good selectivity towards light olefins and excellent anti-sintering performance, especially at high temperature. It was superior to a supported Fe-based catalyst because the Fe particles in Pod-Fe were well protected by the carbon shells. This result provides a practical approach to stabilize metal nanoparticles for reactions at high temperature in heterogeneous catalysis.

References

[22] Raupp GB, Delgass WN J. Catal, 1979, 58: 337
Iron catalyst encapsulated in carbon nanotubes for CO hydrogenation to light olefins

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Pod-like carbon nanotubes with encapsulated iron particles were used as an efficient Fischer-Tropsch catalyst for light olefins, giving high selectivity of light olefins and good stability.