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Monodisperse nano-Fe₃O₄ on α-Al₂O₃ Catalysts for Fischer-Tropsch Synthesis to Lower Olefins: Promoter and Size Effects

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Abstract: The Fischer-Tropsch synthesis to lower olefins (FTO) is a desirable nonpetroleum-based route to produce basic chemicals. A novel two-step method was applied to synthesize iron-based supported catalyst, which is to prepare nano-Fe₃O₄ first by thermal decomposition method and sequentially load them on α -Al₂O₃ by impregnation. TEM and XRD results manifested that the controllable, uniform Fe₃O₄ nanoparticles are monodispersed on the surface of α -Al₂O₃. H₂-TPR demonstrated that the reduction of Fe species was facilitated because of the weak interaction between Fe species and the support. These superior properties contribute to an enhanced catalytic activity and stability, comparing with the catalyst prepared by directly impregnating ammonium iron citrate on α -Al₂O₃. Then, effect

Introduction

Lower olefins (ethylene, propylene, and butylene) are key building blocks of chemical industry for production of polymers, solvents, drugs, cosmetics, detergents, etc.^[1] Traditionally, lower olefins are produced by crude oil cracking. However, high energyconsuming of cracking, dependence of oil reserves and environmental factors are currently spurring exploration of alternative routes for production of lower olefins. Direct conversion of coal-, biomass- and natural gas-derived syngas to lower olefins is a potential nonpetroleum-based route to produce high valuable hydrocarbons.

Iron-based catalysts have been widely explored to direct Fischer-Tropsch synthesis to lower olefins (FTO) for many years.^[1] Despite novel catalysts including OX-ZEO^[2] and cobalt carbide^[3] have been reported to obtain a high lower olefins selectivity with a relative lower CO conversion, iron-based catalysts still arouse much more attention due to their low cost, tolerance for CO/H₂ ratio, resistance to contaminants, and feasibility in industry. Generally, particle size of Fe species,^[4] promoter,^[5-7] Fe precursor^[8] and support^[9, 10] should be taken into account to design iron-based FTO catalyst.

Promoter modification is necessary for iron-based catalysts to gain an appreciable selectivity of lower olefins. Until now, different promoters including transition metals such as manganese^[8], vanadium,^[11] zirconium,^[12] zinc,^[13] alkaline-earth metals such as Mg,^[14] alkali metals such as K^[15, 16] and Na^[5, 13, 17]and non-metallic

of promoters were investigated at the same Fe loading and nanoparticle size. The appropriate addition of K could enhance catalytic activity and suppress secondary hydrogenation. On the contrary, S has a negative impact on CO conversion and greatly decreases C₅₊ selectivity. Particularly, the combination of K and S could obtain more pronounced CO conversion and higher lower olefins selectivity (~40%). Furthermore, the size effects were explored by precisely tailoring the iron oxide particle size, keeping the Fe loading constant. It is found that 12.0 nm nano-Fe₃O₄ on α-Al₂O₃ with or without K plus S promoters showed the best catalytic activity among the catalysts with different particle size.

N^[18] and S^[19-21] have been investigated on CO hydrogenation. Alkali metals are typically additives as electron donor promoters, which facilitate CO adsorption and dissociation and suppress H₂ adsorption and secondary hydrogenation, resulting in an improvement of lower olefin selectivity.^[5, 22] In addition, alkali metals also enhance the activity of water-gas shift (WGS) reaction, which provide an H2-rich environment to accelerate CO conversion.^[16] However, excess alkali metals could cover active sites,[23] resulting in a decline in catalytic activity. The effect of S on FTO remains obscured. Although it was considered as a poison for Fischer-Tropsch catalysts.^[24] recent studies have showed it is able to improve CO conversion, decrease CH4 selectivity [19-21] and increase lower olefins selectivity. [5, 25] De Jong et al.^[5, 26] found the coexistence of Na and S could further increase catalytic activity and lower olefins selectivity than a single promoter do. However, the synergistic effect between S and alkali metals should be further clarified.

CO hydrogenation is a structure-sensitive reaction. Particle size of active phase (e.g. Fe^[6, 7, 27, 28] or Co^[29, 30]) plays a crucial role not only in activity but also in product distribution. However, different results have been obtained due to the diversity of catalyst structure and composition. With respect to FTO on iron-based catalyst, de Jong^[4] found the initial activity increased with the decrease of average iron carbide size from 7 to 2 nm over carbon nanofiber supported catalysts. lablokov et al.[27] reported that the selectivities of CH4 and short-chain olefins decreased with a favorable turnover frequency as Fe particle size increased on Fe/MCF-17 catalyst, unlike the de Jong's results. Therefore, the influence of particle size might depend on the carrier and catalyst preparation method. Until now, particle size of active species is mainly tailored by altering metal loading on support, thus it is difficult to solely establish size effect on catalytic performance without the impact of the amount of active species.

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Conventionally, supported iron-based catalysts in FTO are prepared through impregnation or coprecipitation method. However, it is difficult to obtain Fe nanoparticles with a narrow distribution and uniform interparticle spacing on the support in such methods.^[31] Besides, some work found they also give rise to limited mechanical stability, agglomeration and sintering during calcination, and strong metal-support interaction.[32] On the other hand, Fe₂O₃ is usually detected as the dominate Fe species in catalysts prepared using impregnation or precipitation, which is generally accepted to be reduced to Fe₃O₄ firstly and then transform to iron carbide under syngas atmosphere.^[33] Therefore, Fe₃O₄ often allows an enhanced activity and selectivity of lower olefins in FTO.^[8, 34] Recently, the development of nanomaterials chemistry provides new strategies for catalysts design and fabrication. Some preparation methods (e.g. impregnation of the support with a suspension of nanocrystals in liquid-phase) are applied to obtain the supported catalysts with uniform, singlephase and well-dispersed nanoparticles.

In this work, a novel two-step method was employed to fabricate monodisperse nano-Fe₃O₄ on α -Al₂O₃, in which nano-Fe₃O₄ was prepared by thermal decomposition method and then loaded on the support using impregnation method. We chose α -Al₂O₃ as the substrate, because its weak interaction with Fe species has been proved to be favorable for the reduction and carburization of iron oxides. The obtained catalysts were compared with the ones prepared by one-step impregnation method in terms of physicochemical properties and catalyst performance. Then, the promotion of K and S as additives were considered and discussed based on both experimental and DFT calculations. Moreover, the particle size of Fe₃O₄ was also precisely manipulated under the same loading by controlling the decomposition conditions, in order to solely illuminate size effect on FTO catalytic performance.

Results and Discussion

Comparison with one-step impregnation method

As mentioned above, two-step method was used to obtain nano- Fe_3O_4 supported on α -Al₂O₃ catalyst. A comparative catalyst were prepared by traditional method of impregnating ammonium iron citrate aqueous solutions on α -Al₂O₃. Given in Figure 1, XRD patterns ascertain that Fe₃O₄(12.0) and 0.5K-0.05S-Fe₃O₄(12.0) mainly contain Fe₃O₄ magnetite (JCPDS 19-0629), which is consistent with Zheng's results,^[35] indicating that Fe₃O₄ magnetite nanoparticles could be obtained by thermal decomposition method. The subsequent loading on α -Al₂O₃ doesn't change crystal phase of Fe species (Figure S1), suggesting that the nano-Fe₃O₄ are very stable during impregnation and calcination, even when we manipulate the size of nano-Fe $_3O_4$ and dope K and S as promoters. With respect to one-step impregnation method, a-Fe₂O₃ phase (JCPDS 33-0664) is the predominate species on $Fe_2O_3(12.6)$ and $0.5K-0.05S-Fe_2O_3(12.6)$, which indicates Fe precursor is prone to transform to Fe₂O₃.

The TEM images (Figure 2a-d) demonstrates that uniform nano-Fe₃O₄ could be obtained using thermal decomposition method. And the particle size could be modulated by changing the amount of oleic acid during thermal decomposition procedure.

Particle size statistics shows that the standard deviation from the average diameter is less than 10% for nano-Fe₃O₄ with different particle size. After being impregnated on α -Al₂O₃, nano-Fe₃O₄ is well-dispersed on the support. In contrast, the Fe₂O₃ nanoparticles of Fe₂O₃(12.6) prepared by direct impregnation method distribute unevenly (Figure 2e). Additionally, Table S1 shows the practical Fe loadings of all catalysts are almost the same, and the K contents are also in good agreement with the designed values. This means the new preparation method also provides an excellent way to explore the size effects of Fe-based catalysts under the same metal loading on CO hydrogenation, which will be discussed in detail later.



Figure 1. XRD patterns of Fe $_3O_4(12.0),\ 0.5K-0.05S-Fe _3O_4(12.0),\ Fe _2O_3(12.6)$ and $0.5K-0.05S-Fe _2O_3(12.6).$

H₂-TPR was used to determine the interaction between Fe species and the support. As shown in Figure 3, it reveals that all the catalysts present three peaks with increasing reduction temperature, which are assigned to $Fe_2O_3 \rightarrow Fe_3O_4$, $Fe_3O_4 \rightarrow FeO_4$, $FeO \rightarrow Fe$, respectively. It is noteworthy that there is also a small peak at low temperature for Fe₃O₄(12.0) sample. It might be because nano-Fe₃O₄ is encapsulated by a thin layer of γ -Fe₂O₃, which is formed during calcination at air atmosphere. Park et al.[36] also found the partial oxidation of Fe_3O_4 to γ -Fe₂O₃ occurred when $Fe_3O_4@SiO_2$ was calcined in air. We also found that all the three reduction peaks of Fe₂O₃(12.6) shift towards higher temperatures, comparing with $Fe_3O_4(12.0)$. Besides, $Fe_3O_4(12.0)$ and 0.5K-0.05S-Fe₃O₄(12.0) are completely reduced when temperature arrives at 700 °C while an elevated temperature is requisite for $Fe_2O_3(12.6)$ and $0.5K\text{-}0.05S\text{-}Fe_2O_3(12.6)$ to be reduced to metallic Fe. This indicates the interaction between iron oxides and a-Al₂O₃ of the catalyst prepared by two-step method is weaker than direct impregnating Fe precursors on α -Al₂O₃.

As shown in Figure 4, Fe₃O₄(12.0) significantly outperforms Fe₂O₃(12.6) in CO hydrogenation with the same iron oxide particle size and Fe loading. Furthermore, Fe₃O₄(12.0) shows an excellent stability while the activity of Fe₂O₃(12.6) is slightly decreased. The specific data including conversion, selectivity and O/P ratio at TOS = 30 h are given in Table S2. The superiority

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of Fe₃O₄(12.0) probably results from the fact that Fe₃O₄ could be reduced more easily than Fe₂O₃ because of its weaker interaction with support, which is confirmed by H₂-TPR profiles (Figure 3). In published research, it is generally accepted that Fe₂O₃ as iron carbide precursor is reduced first to Fe₃O₄ and then to iron carbides under CO or syngas atmosphere.^[33, 37]

With the addition of K plus S, both 0.5K-0.05S-Fe₃O₄(12.0) and 0.5K-0.05S-Fe₂O₃(12.6) exhibit enhanced catalytic performance compared with corresponding unpromoted catalysts (Figure 4, Table S2). The effects of K and(or) S on catalytic performance

would be further discussed in next section. But more importantly, the FTY on 0.5K-0.05S-Fe₃O₄(12.0) increases within 15 h and then remains stable within 30 h, indicative of the excellent stability and remarkable activity. On the contrary, 0.5K-0.05S-Fe₂O₃(12.6) catalyst rapidly deactivates after reaching the maximum value at 6 h, showing unfavorable stability when compared with 0.5K-0.05S-Fe₃O₄(12.0). The TEM images of these four used catalysts (Figure 5) evidenced that monodisperse Fe species nanoparticles are maintained with little sintering on Fe₃O₄(12.0) and 0.5K-0.05S-Fe₃O₄(12.0), while a large extent of aggregation is observed on Fe₂O₃(12.6) and 0.5K-0.05S-Fe₂O₃(12.6), which result in the poor stability of Fe₂O₃(12.6) and 0.5K-0.05S-Fe₂O₃(12.6).



Figure 3. H₂-TPR profiles of Fe₃O₄(12.0), 0.5K-0.05S-Fe₃O₄(12.0), Fe₂O₃(12.6) and 0.5K-0.05S-Fe₂O₃(12.6).



Figure 4. Catalytic performance of nano-Fe₃O₄ on α -Al₂O₃ catalysts and comparative experiment prepared by impregnating ammonium iron citrate on α -Al₂O₃ with or without K plus S promoters. (reaction conditions: 340 °C, 1.0 MPa, H₂/CO = 1, WHSV = 27 000 mL·g⁻¹·h⁻¹)



Figure 2. TEM images (inset: nano-Fe₃O₄ before supported) and PSD of nano-Fe₃O₄ on α -Al₂O₃ (a) 8.3 nm, (b) 12.0 nm, (c) 15.2 nm, (d) 17.3 nm and referenced catalyst (e) Fe₂O₃(12.6).



Figure 5. TEM images of used catalyst. (a) $Fe_3O_4(12.0)$, (b) 0.5K-0.05S- $Fe_3O_4(12.0)$, (c) $Fe_2O_3(12.6)$, (d) 0.5K-0.05S- $Fe_2O_3(12.6)$. These catalysts were analyzed after 30 h (inset: PSD histograms of the Fe species nanoparticles).

50

Promoter effects

50 nm

In FTO reaction, promoters are usually essential to make catalyst favorable for producing lower olefins. In this work, K and S were investigated. The promoter was introduced by impregnating promoter precursors on Fe₃O₄(12.0), and ICP results demonstrate all the catalysts with different promoters have almost same Fe loadings (Table S1).

The results of catalyst performance are summarized in Figure 6, 7 and Table S2. Although $Fe_3O_4(12.0)$ shows a stable activity in 30 h, a low selectivity to lower olefins (28.2%) with high CH₄ content (26.9%) is obtained. The addition of appropriate amount of K increases the FTY by more than 100%. As reported in literature, K as an additive could facilitate CO activation, which leads to activity improvement. Further improving K content might cover active sites.^[15, 23] Meanwhile, CH₄ formation is suppressed with the increased molar ratio of olefin to paraffin, demonstrating that K additive inhibits the secondary hydrogenation.[38] On the contrary, the catalyst with S additive shows a decreased activity by almost 50% compared with Fe₃O₄(12.0), accompanied with enhanced CH₄ selectivity (from 26.9% to 35.1%) and suppressed C₅₊ formation (from 32.9% to 14.0%). These results reveal that the growth of carbon chain is restrained due to S addition. In published work, the effect of S additive is controversial. De Jong's group^[5] found that a small amount of S could enhance the catalytic activity and decrease CH₄ production apparently, while Xu et al.^[39] proposed that S poisoned Fe/α-Al₂O₃ catalyst by interfering CO dissociation. Here, it is interesting that when S is added with K, a remarkable improvement of activity is observed, over three times than unpromoted catalyst, even higher than K as sole promoter.

Besides, a higher lower olefins selectivity (40.8%) is obtained owing to a decreased CH_4 formation rate. We also note that the addition of K plus S makes the induction period become longer and the activity doesn't decline after 30 h on stream. By optimizing



Figure 6. Catalytic performance with time on stream of nano-Fe₃O₄ on α -Al₂O₃ catalysts with different promoters. (reaction conditions: 340 °C, 1.0 MPa, H₂/CO = 1, WHSV = 27 000 mL·g⁻¹.h⁻¹)



Figure 7. Product selectivity of nano-Fe₃O₄ on α -Al₂O₃ catalysts with different promoters. (reaction conditions: 340 °C, 1.0 MPa, H₂/CO = 1, WHSV = 27 000 mL·g⁻¹·h⁻¹, TOS= 30 h)

the content of K and S, 0.5K-0.05S-Fe₃O₄(12.0) shows superior catalytic features.

Considering product selectivity is sensitive to CO conversion for FTO,^[40] we conducted some experiments by maintaining CO conversion of ~10% under different space velocity (Table S3). It is concluded that impacts of K and (or) S on product distribution are similar with the results discussed above. It is noteworthy that a higher lower olefins selectivity (53.5%) is obtained for 0.5K-0.05S-Fe₃O₄(12.0) at CO conversion of 13.5%, which are superior to most published work.^[9, 18, 25]

The TEM images illustrate that all the used catalysts exhibit uniform Fe species with similar particle size (seen in Figure S2), although a little aggregation of Fe species occurs during the reaction. This reconfirms promoter effect is discussed under exclusion of the influence of particle size in our work. It is noteworthy that a core-shell structure of particles emerges after FTO reaction, particularly on catalysts with K or dual promoters.

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At the core of particle, visible lattice fringes with d-spacing of 0.205 nm is measured, corresponding to the (510) lattice planes of Fe₅C₂ (Figure S3a). These indicate that K or dual promoters facilitate the extent of carburization. Electron Energy Loss Spectroscopy (EELS) (Figure S3b–f) also demonstrated that the core is rich in iron and carbon while the shell is mainly iron oxide, which is in accordance with de Jong's results.^[6] Besides, Fe₅C₂ phase is also verified from XRD patterns (Figure S4) and XPS spectra (Figure S5) for Fe₃O₄(12.0) and 0.5K-0.05S-Fe₃O₄(12.0). We also found K and S cannot be detected due to the small amount, thus STEM-EDS (Figure S6) was employed to determine the spatial distribution of K and S. Both of them are dispersed evenly on the support and the content of K is much more than S. These results provide reference for the following DFT calculations.



Figure 8. Top and side views of CO adsorption on the Fe_5C_2 (510) surface doped by promoters. Atom key: Fe(blue), C(gray), K(purple), S(yellow), and O(red).

DFT calculations was also used to explore the effect of different promoters on catalytic performance. According to the above characterizations and literature,[41, 42] we calculate the CO adsorption energy on Fe_5C_2 (510) surface with addition of K and/or S (Figure 8). The adsorption energies and bond lengths of C-O are summarized in Figure 8. Comparing with the catalyst without promoter, the addition of K makes the CO adsorption more stable. Accordingly, the C-O bond is elongated from 1.205 Å to 1.227 Å. On the contrary, the presence of S results in a most unstable configuration with a distance between the C and O atom in CO of 1.117 Å. With the coexistence of K and S (Figure 8d, 1K1S promoted), CO adsorption is also enhanced than unpromoted and the corresponding C-O bond length in this configuration is 1.225 Å. Furthermore, we considered the coverage effect of promoters. CO adsorption on Fe_5C_2 (510) surface with different K and S compositions was calculated. Increasing the K/S ratio gradually strengthens the CO adsorption. The investigation about calculation methods (Table S4) shows that, although the structural parameters and adsorption energies differ because of methods, the variation trends caused by promoters behave similarly. In both published and this work, a synergistic effect of alkali metals and S always contain much more K than S. Therefore, our calculation results are in accordance with experimental findings. It can be concluded that K promoter facilitates the adsorption and activation of CO while S addition makes it become more difficult, and a synergy is emerged when K and S coexists on the surface of catalysts.

Size effects

As reported in literature, the particle size of Fe species plays an important role in CO hydrogenation. By the two-step preparation method, particle size of Fe_3O_4 on α -Al₂O₃ can be manipulated precisely in the range of 8~18 nm, no matter weather promoter is introduced. Before discussing the effect of Fe species particle size on catalytic performance of CO hydrogenation, we have measured the particle sizes of the used catalysts with and without dual promoters from the TEM images (Figure S7). After reaction, the Fe species possess similar particle sizes with the corresponding fresh catalysts, even undergoing complex phase changes. It confirms that no agglomeration of Fe nanoparticle occurred during reaction, which results in almost constant FTYs over the catalysts with different sizes. Upon introduction of dual promoters, the sizes of Fe species slightly increase, but the variation trend is still maintained. Therefore, the investigation and discussion about size effect are carried out under the premise of the Fe species with nearly invariable particle size.

For $Fe_3O_4(x)$, it is noted from Figure 9 that the initial FTY increases first and then decreases with the increase of Fe₃O₄ particle size from 8.3 nm to 17.3 nm and 12.0 nm Fe₃O₄ exhibits the highest catalytic activity. The products distribution is also influenced by particle size. It is observed from Table 1 that although little difference exists on lower olefins selectivity (~30%), lower alkanes (9%) and oxygenates (4%), the variation trend of C_{5+} selectivity is coincident with FTY, which is contrary to CH_4 selectivity. Fe₃O₄(12.0) displays the highest C₅₊ selectivity in combination with the lowest CH₄ selectivity. The shape-sensitivity of iron-based catalysts for FTO has been reported by several research groups. De Jong et al.^[4] found that the initial activity decreased when Fe_5C_2 size increased from 2 to 7 nm and further increase of particle size had negligible impact on FTY. Kruse's reported that the catalytic activity of Fe(0)/MCF-17 silica increased with the increase of Fe particle size in the range of 1.8 ~ 9.0 nm.^[27] Besides, other different results were obtained for ironbased catalyst supported on AC or Al₂O₃. Due to the different catalyst preparation and composition, the metal-support interaction differs a lot, which might mask the influence of particle size.^[4, 27] Even both on α-Al₂O₃, Fe₂O₃(12.6) prepared by impregnation of Fe precursor exhibits a much lower FTY compared to Fe₃O₄(12.0) with similar particle size in our work. This comparative experiment evidences the above deduction. On the other hand, the seemingly controversial results also might be caused by different investigated range of particle size. Therefore, it is necessary to investigate the size effect for novel catalysts, especially prepared by new methods.

For catalysts with dual promoters, FTYs present similar trend with increasing Fe species particle size, although the values are four times higher than unpromoted catalysts. However, the impact of size on product distribution is almost nil, showing appreciable lower olefins formation (~40%) and low CH_4 contents (~14%). FULL PAPER

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Catalyst	CO Conv. [%]	FTY [10 ⁻⁶ mol _{CO} g _{Fe} ⁻¹ s ⁻¹]	TOF _{Fe5C2} [s ⁻¹]	CO2 Sel. [%]	Hydrocarbon Sel. [%]					
					CH₄	C ₂₋₄ °	C ₂₋₄ =	C ₅₊	Oxy. ^[b]	0/P ^[0]
Fe ₃ O ₄ (8.3)	6.1	108	0.025	32.4	31.1	9.1	32.7	23.2	4.0	3.6
Fe ₃ O ₄ (12.0)	10.1	178	0.062	28.9	26.9	8.7	28.2	32.9	3.3	3.4
Fe ₃ O ₄ (15.2)	6.2	111	0.047	30.9	29.9	8.0	32.1	26.0	3.9	4.0
Fe ₃ O ₄ (17.3)	4.3	61	0.031	28.0	39.5	8.7	30.6	17.9	3.2	3.5
0.5K-0.05S-Fe ₃ O ₄ (8.3)	25.7	465	0.083	47.4	10.5	4.3	39.5	39.8	5.9	9.2
0.5K-0.05S-Fe ₃ O ₄ (12.0)	30.9	541	0.128	51.6	14.3	5.6	40.8	32.5	6.8	7.3
0.5K-0.05S-Fe ₃ O ₄ (15.2)	27.0	486	0.151	49.7	12.6	4.6	39.3	37.4	6.1	8.5
0.5K-0.05S-Fe ₃ O ₄ (17.3)	27.6	477	0.178	47.0	13.8	5.0	37.0	38.9	5.4	7.4

Table 1. Catalytic Performance of nano-Fe₃O₄ on α-Al₂O₃ catalysts of different sizes with and without K plus S promoters under FTO conditions^[a]

[a] Reaction conditions: T = 340 °C, P = 1.0 MPa, $H_2/CO = 1$, WHSV = 27 000 mL·g⁻¹·h⁻¹, TOS = 30 h;

[b] Oxygenates; [c] The molar ratio of olefin to paraffin in the C₂~C₄ hydrocarbons.

To further understand the effect of active phase size on catalytic performance, the bulk rates were converted to TOFs based on Fe_5C_2 and Fe. respectively (Table S5). The calculation method is introduced in the Supporting Information. It was found that results based on Fe and Fe_5C_2 are very similar and follow the same trend. The estimated TOF based on Fe₅C₂ model was plotted as a function of Fe₃O₄ particle size with and without K plus S promoters (Figure 10). It is found that for unpromoted catalysts. TOF varied almost identically to FTY. It indicates that shape-features such as terrace, edge, dominate catalytic performance. It is interesting that for the catalysts with K plus S promoters, TOF increases proportionately to particles size, unlike the FTY variation. For larger Fe₃O₄ particle, it can be predicted that stepped-like sites are less than terraced-like sites and K plus S promoters are more likely to be stabilized on terraced-like sites, which might enhance the possibility of synergy between K and S. Therefore, we conclude that the synergetic promoting effect of K and S results in a remarkable enhancement of activity, which compensate or even mask the influence of particle size.



Figure 9. FTY as a function of Fe₃O₄ particle size with and without K plus S promoters. (reaction conditions: 340 °C, 1.0 MPa, H₂/CO = 1, WHSV = 27 000 mL-g⁻¹·h⁻¹, TOS=30 h).



Figure 10. TOF as a function of Fe₃O₄ particle size with and without K plus S promoters. (reaction conditions: 340 °C, 1.0 MPa, $H_2/CO = 1$, WHSV = 27 000 mL·g⁻¹·h⁻¹, TOS=30 h).

Conclusions

In summary, a novel two-step method (thermal decomposition and then impregnation) was employed to fabricate monodisperse nano-Fe₃O₄ on α -Al₂O₃. In comparison with direct impregnation method, the catalysts prepared by the two-step method exhibit more uniform, well-dispersed and stable Fe₃O₄ nanoparticles. Meanwhile, the weaker interaction between Fe species and support enables the reduction of Fe phase more facile. These superior properties lead to an enhanced activity and excellent stability in FTO. Though modulating the amount of oleic acid in the first thermal decomposition step, the catalysts with different size of Fe₃O₄ could be engineered, which is propitious to investigate promoter effect under the same Fe loading and particle size. K additive in appropriate amount, facilitates CO adsorption and activation and suppress secondary hydrogenation.

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As a result, a greatly improved CO conversion is obtained with a lower CH₄ selectivity and more favorable lower olefins selectivity. On the contrary, the sole presence of S leads to a decline in FTY and increase CH₄ formation. Interestingly, when S is combined with K, the improvement of CO conversion become more pronounced, owing to an enhanced CO activation, which is confirmed by DFT calculation. On the other hand, it is found that size of nano-Fe₃O₄ has an impact on FTO performance under the same Fe loading. Furthermore, with or without K plus S promoters, the impact is similar. Among the catalysts with different particle size, 12.0 nm nano-Fe₃O₄ on α -Al₂O₃ shows the best catalytic activity. The characterization of used catalysts shows that, little agglomeration occurs during the FTO reaction, which provides a good support of the exhibited excellent stability.

Experimental Section

Materials

1-Octadecene (>90%), Oleic acid (>90%), iron (III) chloride were purchased from Aladdin. Potassium carbonate (>99%) was purchased from Kewei Co. of Tianjin University. Iron (II) sulfate heptahydrate (>99.5%) was purchased from Tianjin Kermel Co. LTD of China. Ammonium iron citrate with analytical reagent grade was purchased from Guangfu Fine Chemical Co. LTD of Tianjin. Sodium oleate, ethanol, hexane, and cyclohexane are of analytical reagent grade, purchased from YuanLi Chemical Reagent Co., LTD. All the reagents were used without further purification. α-Al₂O₃ were obtained by calcining AlOOH, purchased from Nankai University Catalyst Co., at 1200 °C for 4 h with a heating ramp of 2 °C·min⁻¹ from 40 °C to 1000 °C and then a heating ramp of 1 °C·min⁻¹ from 1000 °C to 1200 °C.

Catalyst Preparation

Nano-Fe₃O₄ were prepared using thermal decomposition method^[43, 44] with some modifications. In a typical synthetic procedure of 12.0 nm nano-Fe₃O₄, 6.5 g of iron (III) chloride and 36.5 g of sodium oleate were dissolved in a mixture solvent composed of 80 mL ethanol, 64 mL deionized water and 140 mL hexane. The resulting solution was heated to 60 °C, refluxed for 4 h, and then separated by a separating funnel. The organic layer containing Fe(oleate)₃ complex was collected, washed with 100 mL deionized water, and then the excess solvent was removed by reduced pressure distillation. Subsequently, the $Fe(oleate)_3$ complex was dispersed in a mixture of 3.0 g oleic acid and 100 g 1-octadecene. The mixture solution was stirred under Ar flow for 30 min at 120 °C, and then heated to 320 °C with a heating rate of 3.3 °C·min⁻¹, and refluxed for 30 min. The resulting solution containing the nanocrystals was then cooled to room temperature, and 250 mL of ethanol was added to the solution to precipitate the nanocrystals and the supernatant was decanted. The nanocrystals were dispersed in the mixture of hexane and ethanol, and then separated by centrifugation. The redispersion-centrifugation process was repeated for several times and finally dispersed in 250 mL of cyclohexane. By altering the amount of oleic acid, 8.3 nm, 15.2 nm, and 17.3 nm nano-Fe₃O₄ were obtained, respectively.

For the preparation of nano-Fe₃O₄ on α -Al₂O₃ (10wt.% Fe), 4.0 g α -Al₂O₃ was added in 150 mL Fe₃O₄ solution prepared above. After stirring 24 h under room temperature, cyclohexane was removed by reduced pressure distillation. The dried catalysts were treated under air flow (100 mL·min⁻¹) at 350 °C for 4 h with a heating ramp of 5 °C·min⁻¹. The supported catalysts were denoted as Fe₃O₄(x), in which x refers to the different particle sizes.

The K-Fe₃O₄(12.0) catalysts was prepared by impregnating Fe₃O₄(12.0) with K₂CO₃. Calculated mass of K₂CO₃ was dissolved in 50 mL deionized water. Then, 1.0 g Fe₃O₄(12.0) was added to the solution and stirred at room temperature for 12 h, excess water was evaporated under reduced pressure. The solid was then dried at 120 °C for 8 h. The as-prepared K-Fe₃O₄(12.0) catalysts are denoted as 0.5K-Fe₃O₄(12.0), 1.0K-Fe₃O₄(12.0), in which the numbers before K stand for K contents of 0.5, 1.0 wt.%, respectively.

The 0.05S-Fe₃O₄(12.0) catalyst was prepared by impregnating Fe₃O₄(12.0) with FeSO₄·7H₂O, similar with K-Fe₃O₄(12.0). After dried at 120 °C for 8 h, the sample was calcined at 500 °C with a heating ramp of 5 °C·min⁻¹ for 2 h under air flow.

The K-S-Fe₃O₄(12.0) catalyst was prepared by co-impregnating Fe₃O₄(12.0) with K₂CO₃ and FeSO₄·7H₂O. The procedure was in consistent with the process as described for the preparation of 0.05S-Fe₃O₄(12.0). K-S-Fe₃O₄(12.0) catalysts are denoted as 0.5K-0.05S-Fe₃O₄(12.0), 0.5K-0.10S-Fe₃O₄(12.0), in which the numbers stand for the nominal K and S percent contents, respectively. Similarly, 0.5K-0.05S-Fe₃O₄(17.3) were obtained by impregnating Fe₃O₄(8.3), Fe₃O₄(15.2), Fe₃O₄(15.2), Fe₃O₄(17.3) with K₂CO₃ and FeSO₄·7H₂O, respectively.

As references, the Fe₂O₃(12.6) catalyst was prepared by impregnating α -Al₂O₃ with ammonium iron citrate. 3.2 g ammonium iron citrate was dissolved in 100 mL deionized water. Then, 4.0 g α -Al₂O₃ was added to the solution and stirred at room temperature for 24 h, excess water was evaporated under reduced pressure. The catalyst was dried and calcined using the same procedure as described for the 0.05S-Fe₃O₄(12.0). The 0.5K-0.05S-Fe₂O₃(12.6) catalyst were prepared by impregnating Fe₂O₃(12.6) with K₂CO₃ and FeSO₄-7H₂O. The procedure was in consistent with the process as described for the preparation of K-S-Fe₃O₄(12.0).

Catalyst characterization

An inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista-MPX) was used to analyze the Fe and K content of samples.

The powder X-ray diffraction (XRD) characterization was performed on a RigakuD/max-2500 diffractometer with a CuK α radiation (40 kV, 200 mA) (λ = 0.15418 nm). The fresh catalyst was scanned at 8°·min⁻¹ from 10° to 90°, while the used catalyst was scanned at 1°·min⁻¹ from 30° to 50°.

The morphology and particle size of sample was characterized with a FEI Tecnai G2F20 transmission electron microscope (TEM) at 200 kV. The samples were prepared by directly dropping cyclohexane solution containing nano-Fe₃O₄ on carbon-coated copper grid. Other samples was prepared by ultrasonic dispersion in ethanol and then the suspension was dropped onto a carbon-coated copper grid. Particle size distribution (PSD) histograms were constructed by randomly measuring for more than 300 nanoparticles.

Hydrogen temperature-programmed reduction (H₂-TPR) profiles of the asprepared catalysts were obtained using a Micromeritics AutoChem 2910 equipped with a TCD detector. About 0.05 g of the fresh catalyst was pretreated in Ar flow at 200 °C for 1 h, and then cooled to 60 °C. The TPR measurement was conducted by heating the sample to 800 °C with a ramp of 10 °C·min⁻¹ in a flow of 10 vol% H₂/Ar (30 mL·min⁻¹).

X-ray photoelectron spectroscopy (XPS) was conducted using PHI-1600 ESCA XPS equipment with monochromated Mg-K α X-ray radiation. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.

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Catalytic Test

The FTO performance of as-prepared catalyst was conducted in a fixedbed stainless steel tubular reactor (8.0 mm inner diameter). For all the experiments, 0.2 g catalyst (40-60 mesh) mixed with 1.0 g quartz sand (40-60 mesh) were loaded into the reactor. Prior to the reaction, the catalyst was reduced with pure H2 at 350 °C at a flow rate of 90 mL·min⁻¹ for 2 h under atmospheric pressure. Catalytic testing was performed under 340 °C, 1.0 MPa, and a gaseous mixture of 90 vol.% syngas (V(H₂): V(CO) =1) and 10 vol.% Ar (as internal standard substance for quantitative analysis) with a flow rate of 100 mL·min⁻¹. The reaction products were passed through a hot trap at 145 °C. The uncondensed gas was reduced to atmospheric pressure by a back pressure valve, and then analyzed by an Agilent 7890B GC equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) for online analysis. Ar, CO, CH4, and CO₂ were analyzed by an UltiMetal column connected to the TCD. The hydrocarbons were analyzed by a 19091P-S12 25m x 0.32mm x 8um HP-AL/S column connected to the FID. The catalytic activity was evaluated by FTY (mol of converted CO per gram of Fe per second). TOF was estimated by assuming the iron-containing particles consist fully of Fe_5C_2 and 14Fe atoms nm^{-2.[4]} The diameter of Fe_5C_2 could be calculated from the particle size of Fe₃O₄ according to the density of Fe₅C₂ (ρ = 7.57 g·mL⁻¹) and Fe₃O₄ (ρ = 5.18 g·mL^-1). The selectivity to hydrocarbon was calculated on carbon basis with the exception of CO2. Proper passivation was conducted before exposure to air for characterizing the used catalyst.

DFT Calculations

Cambridge sequential total energy package (CASTEP)^[45] was used to perform Periodic DFT calculations. The interaction between electrons and atomic cores were calculated by three gradient-corrected exchange correlation (GGA) method and the exchange-correlation energy was described using Perdew-Burke-Ernzerhof (PBE) functional.^[46] The Kohn-Sham equation expanded in a plane wave basis was set up to 400 eV.^[47] The convergence criteria for structure optimization and energy calculation were set to medium quality with the tolerance for SCF, energy, maximum force, and maximum displacement of 2.0×10^{-6} eV-atom⁻¹, 2.0×10^{-5} eV- Δ^{-1} and 2.0×10^{-3} eV- Δ^{-1} , respectively. Without counting the adsorbates, slab vacuum was set to span a range of 10 Å to minimize the interactions between the periodic slabs.

The adsorption energy is defined as $E_{ads} = E_{(adsorbates+slab)}-(E_{slab} + E_{adsorbates})$, where $E_{(adsorbates+slab)}$ is the total energy of the slab with adsorbates, E_{slab} is the energy of the corresponding bare slab, and $E_{adsorbates}$ is the total energy of free adsorbates in gas phase. Basically, the more negative E_{ads} is, the stronger species were adsorbed.

Bulk χ -Fe₅C₂ has C2/c crystallographic symmetry and per unit cell contains 20 Fe atoms and 8 C atoms. χ -Fe₅C₂ (510) surface model contains eight Fe layers and all adsorbents were put on only one side of the slab.^[41] A p(2x1) supercell slab consisting of 40 Fe atoms and 16 C atoms in a unit cell was chosen, in which one layered Fe and two layered C are fixed in the bottom of their bulk positions, while the one Fe layer and two carbon layers on the top can relax, the 2 x 2 x 1 Monkhorst-Pack k-point mesh were chosen.

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Monodisperse nano-Fe₃O₄ on α-Al₂O₃ Catalysts for Fischer-Tropsch Synthesis to Lower Olefins: Promoter and Size Effects



New method to fabricate monodisperse nano-Fe $_3O_4$ on $\alpha\text{-Al}_2O_3$ catalyst in FTO

A novel two-step method was applied to synthesize monodisperse nano-Fe₃O₄ on α-Al₂O₃, showing enhanced activity and stablity for Fischer-Tropsch synthesis to lower olefins. The engineered catalysts shed light on the effects of promoter (i.e. K and S) and size by eliminating the interference of other factors, such as Fe loading and phase transformation.