A manganese modified Fe_3O_4 microsphere catalyst with effective active phase of forming light olefins from syngas

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Abstract: A manganese modified Fe_3O_4 microsphere catalyst was developed, which effectively converts the syngas to light olefins (C_2-C_4) with selectivity up to 60.1% in all hydrocarbon products. This non-porous catalytic material with fine dispersed manganese contributes to clarifying the different role of iron carbides by solely modifying the carburization of the catalysts and reducing the diffusion resistance of products. Combining various characterization results, including XAFS and Mössbauer Spectroscopy, it is found that the electronic state of surface carbonaceous species was affected by the Mn promoter, leading to the formation of special iron carbide (θ-Fe_3C) and the reactivity for light olefins formation was highly dependent on the content of θ-Fe_3C.

Keywords: Fischer-Tropsch synthesis, light olefins, iron carbide.

1. Introduction

Light olefins (C_2-C_4) are key building blocks of the chemical industry and typically produced by steam cracking naphtha.[1] The direct conversion of syngas into light olefins via the Fischer-Tropsch synthesis (FTS) process is a promising route to meet the increasing demand for chemical feed-stocks.[2] It is well know that iron carbide is recognized as the active phase for the FTS reaction.[3] However, the exact role of different iron carbide phase in the formation of light olefins remains unclear. Herein, a manganese modified Fe_3O_4 microsphere catalyst was developed as illustrated in Figure 1A, where the MnO_x dispersed on the surface of Fe_3O_4 microsphere to avoid the porous structure and solely modify the carburization of the catalysts. It was estimated that this new designed catalyst would improve the light olefins selectivity by alleviating secondary reactions and tuning the properties of surface carbonaceous species.

2. Experimental

The Fe_3O_4 microspheres were prepared by a solvothermal method.[4] For preparation of Mn/Fe_3O_4 catalyst, in order to improving the dispersion of supported Mn, an ethylene glycol solution of $Mn(NO_3)_2$•$4H_2O$ was impregnated onto the Fe_3O_4 microspheres,[5] followed by drying at 473 K under vacuum. The obtained catalysts were characterized by SEM, STEM-Mapping, HRTEM, XRD, N_2-physisorption, XAFS, XPS, H_2-TPR, and Mössbauer spectroscopy.

3. Results and discussion

Figure 1B shows SEM image of the Fe_3O_4 microspheres, which possess uniformly spherical shape of ~300 nm. N_2 adsorption-desorption isotherms show representative type-Ⅱ curves, which is normally obtained with non-porous adsorbents[6]. Meanwhile, it was found that the MnO_x located at the edge of Fe_3O_4 microspheres as shown in Figure 1C. Hence, MnO_x should locate on the surface of the Fe_3O_4 microspheres as designed, and diffusion limitation in the conventional catalysts can be ignored in this catalyst system. It is considered that this unique promoter-on-iron structure of obtained catalyst would contribute to enhancing the promotional effects of manganese and clarifying the different role of iron carbides.

The prepared Fe_3O_4 microsphere catalysts were applied to FTS reaction for 50 h under 1.0 MPa, 593 K, and H_2/CO ratio of 1. The Mn/Fe_3O_4 catalyst with moderate amount of Mn (6 wt %) exhibits the best C_2-

C_4 olefins selectivity (60.1 %) and lowest CH_4 selectivity (9.7 %) with relative better stability compared with un-promoted Fe_3O_4 catalyst. The unprecedented efficiency of converting syngas to light olefins could be attributed to the special surface carbonaceous species, as confirmed by in situ XPS. The results on the activated catalysts show that the presence of significantly different surface carbonaceous species, and the charge of surface carbon atom was influenced by the Mn promoter. It is proposed that a specific carbide phase could be formed on the surface of Fe_3O_4 microsphere due to the presence of Mn promoter. This is also confirmed by Mössbauer spectroscopy and EXAFS. As shown in Mössbauer spectroscopy, a new carbide phase, identified as cementite (θ-Fe_3C), was discerned when Mn was added. Fourier transforms of the EXAFS spectra at the Fe K-edge (Figure 1D) show that, the slightly shorter Fe-Fe bond distance (~1.8 Å) for the Mn-promoted catalysts suggests that the Fe formed another carbide phase, θ-Fe_3C, in addition to χ-Fe_5C_2.[7] The density functional theory (DFT) calculation results indicating that the Fe_3C phase has relatively weak hydrogenation activity for unsaturated hydrocarbon.[8] Thus, it is reasonable to conclude that the θ-Fe_3C phase plays crucial roles in enhancing the light olefins selectivity.

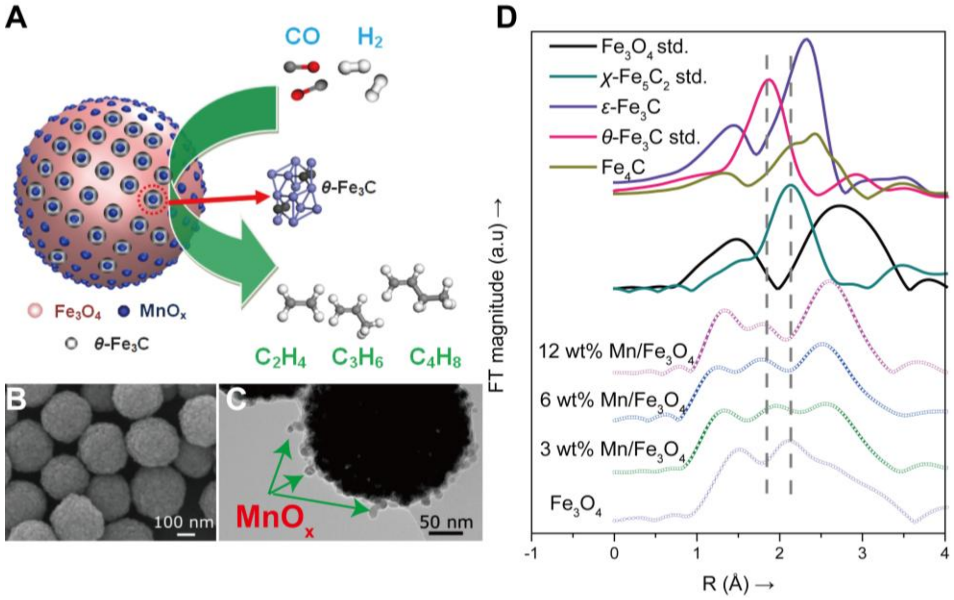

Figure 1. (A) Structural model for the Mn/Fe_3O_4 catalyst; **(B)** SEM images of the fresh Fe_3O_4 microspheres; **(C)** TEM images of the 6 wt % Mn/Fe_3O_4 catalyst after reduction; **(D)** Fourier transformed (FT) k^3-weighted χ(k)-function of the EXAFS spectra. Solid lines denote reference samples of Fe_3O_4, χ-Fe_5C_2, ε-Fe_3C, θ-Fe_3C and Fe_4C. All the pre-reduced catalysts were re-reduced in-situ in syngas (CO/H_2=1) at 623 K for 1 hour.

4. Conclusions

In summaries, the non-porous structure combined with dispersed manganese on the Fe_3O_4 microsphere surface contributes to enhancing the promotional effects of Mn and clarifying the different role of iron carbides. It was found that the θ-Fe_3C plays important role to enhance the selectivity of C_2-C_4 olefins during the FTS reaction, comparing to other iron carbides. In addition, this novel catalytic system proposes a new approach for obtaining a better understanding the promotional mechanisms of the promoters.

References

1. B. Hu, S. Frueh, H. F. Garces, L. Zhang, M. Aindow, C. Brooks, E. Kreidler, S. L. Suib, Appl. Catal. B 132-133 (2013) 54.
2. H. M. T. Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A.I. Dugulan, K.P. de Jong, Science. 335 (2012) 835.
3. S. Li, R. J. O’Brien, G. D. Meitzner, H. Hamdeh, B. H. Davis, E. Iglesia, Appl. Catal. A 219 (2001) 215.
4. J. Liu, Z. K. Sun, Y. H. Deng, Y. Zou, C. Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li, D. Y. Zhao, Angew. Chem. Int. Ed. 48 (2009) 5875.
5. Y. Liu, J. F. Chen, J. Bao, Y. Zhang, ACS Catal. 5 (2015) 3905.
6. K. S. W. Sing, Pure. Appl. Chem. 57 (1985) 603.
7. E. de Smit, A. M. Beale, S. Nikitenko, B. M. Weckhuysen, J. Catal. 262 (2009) 244.
8. C. F. Huo, Y. W. Li, J. Wang, H. Jiao, J. Am. Chem. Soc. 131 (2009) 14713.