**A Manganese Modified Fe3O4 Microsphere Catalyst with Effective Active Phase of Forming Light Olefins From Syngas.**

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**Highlights**

* The MnOx dispersed on the surface of Fe3O4 microsphere.
* The unique promoter-on-iron structure of obtained catalyst.
* The θ-Fe3C phase plays crucial roles in enhancing the light olefins selectivity.

**1. Introduction**

Light olefins (C2-C4) 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]. Herein, a manganese modified Fe3O4 microsphere catalyst was developed as illustrated in **Figure 1A**, where the MnOx dispersed on the surface of Fe3O4 microsphere to avoid the porous structure and solely modify the carburization of the catalysts.

**2. Methods**

The Fe3O4 microspheres were prepared by a solvothermal method [4]. For preparation of Mn/Fe3O4 catalyst, in order to improving the dispersion of supported Mn, an ethylene glycol solution of Mn(NO3)2•4H2O was impregnated onto the Fe3O4 microspheres [5], followed by drying at 473 K under vacuum. The obtained catalysts were characterized by STEM-Mapping, HRTEM, XAFS, XPS, and Mössbauer spectroscopy.

**3. Results and discussion**

**Figure 1B** shows SEM image of the Fe3O4 microspheres, which possess uniformly spherical shape of ~300 nm. N2 adsorption-desorption isotherms show representative type-Ⅱ curves, which is normally obtained with non-porous adsorbents [6]. Meanwhile, it was found that the MnOx located at the edge of Fe3O4 microspheres as shown in **Figure 1C**. Hence, MnOx should locate on the surface of the Fe3O4 microspheres as designed. 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 Fe3O4 microsphere catalysts were applied to FTS reaction for 50 h under 1.0 MPa, 593 K, and H2/CO ratio of 1. The Mn/Fe3O4 catalyst with moderate amount of Mn (6 wt %) exhibits the best C2-C4 olefins selectivity (60.1 %) and lowest CH4 selectivity (9.7 %) with better stability compared with un-promoted Fe3O4 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 Fe3O4 microsphere due to the presence of Mn promoter. This is also confirmed by Mössbauer spectroscopy and EXAFS. As shown in Mössbauer spectroscopy (Figure 2), a new carbide phase, identified as cementite (*θ*-Fe3C), was discerned when Mn was added. Fourier transforms of the EXAFS spectra at the Fe K-edge **(Figure 1D)** show that, the Fe formed another carbide phase, *θ*-Fe3C, in addition to *χ*-Fe5C2. Thus, it is reasonable to conclude that the *θ*-Fe3C phase plays crucial roles in enhancing the light olefins selectivity.



**Figure 1** (A) Structural model for the Mn/Fe3O4 catalyst; (B) SEM images of the fresh Fe3O4 microspheres; (C) TEM images of the 6 wt % Mn/Fe3O4 catalyst after reduction; (D) Fourier transformed (FT) k3-weighted χ(k)-function of the EXAFS spectra. Solid lines denote reference samples of Fe3O4, χ-Fe5C2, ε-Fe3C, θ-Fe3C and Fe4C.



**Figure** **2** Mössbauer spectra of the iron-based catalysts after reduction.

**4. Conclusions**

The non-porous structure combined with dispersed manganese on the Fe3O4 microsphere surface contributes to enhancing the promotional effects of Mn and clarifying the different role of iron carbides. It was found that the *θ*-Fe3C plays important role to enhance the selectivity of C2-C4 olefins during the FTS reaction.

**References**

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