

## One-Pot Solvothermally Synthesized $\text{MFe}_2\text{O}_4$ (M=Fe, Mn, Co, Ni) Microspheres as Catalysts for Fischer-Tropsch to Olefins

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### Highlights

- One-pot solvothermal synthesis of ordered bimetallic ferrite microsphere FTO catalysts.
- Optimum Fe/Mn ratio obtained for ferrite catalysts in terms of the best FTO performance.
- In-depth structure-performance relationships of different ferrite microsphere catalysts.

### 1. Introduction

The Fischer-Tropsch to Olefins (FTO) process offers routes to produce lower olefins directly from coal, biomass or natural gas derived syngas. For coal- or biomass-related feedstocks, iron-based catalysts are especially suited owing to their high olefin selectivity in a broad range of tolerable temperatures and  $\text{H}_2/\text{CO}$  ratios. The performance of iron-based FTO catalysts is sensitive to precursors, promoters and the catalyst structure [1]. However, the traditional co-precipitation method is difficult to prepare promoted catalysts with the crystal phase of the precursor well-modulated and the particle size precisely controlled.

In this work, homogeneous, monodisperse bulk iron-based FTO catalysts were prepared via a facile one-pot solvothermal route. A series of spinel bimetallic ferrite ( $\text{MFe}_2\text{O}_4$ , where M is Fe, Mn, Co or Ni) microsphere catalysts were synthesized and tested under FTO conditions. The catalysts' structure during reduction and reaction were thoroughly studied by multiple in/ex situ characterization techniques. The effect of the doped metal on the preparation, reduction and reaction of the catalyst was illustrated, and the structure-performance relationships of different microsphere catalysts were established.

### 2. Methods

The  $\text{MFe}_2\text{O}_4$  microspheres were prepared using a solvothermal method [2, 3]. Salts of iron and the other metal were first dissolved in ethylene glycol and stirred. Then, sodium acetate was added and the mixture was stirred vigorously for another one hour. Solvothermal synthesis was carried out in a Teflon lined stainless-steel autoclave at 200 °C for 8 h. The solid products were washed with ethanol and water, collected by magnet, and vacuum-dried at room temperature.

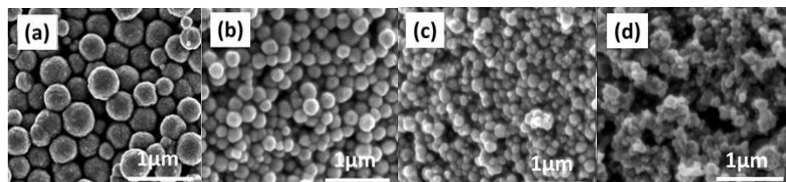
Structural properties and phase states of fresh and spent catalysts were analyzed comprehensively with the help of SEM, Raman, XRD, XPS and Mossbauer spectroscopy. The reduction behavior was studied by combining  $\text{H}_2$ -TPR experiments and in-situ XRD measurements carried out in the  $\text{H}_2$  atmosphere.

The FTO reaction was performed in a stainless steel fixed-bed micro-reactor. The catalysts were reduced with  $\text{H}_2$  prior to the reaction. All products were analyzed by on-line gas chromatograph.

### 3. Results and discussion

Figure 1 shows the morphology of fresh catalysts. The ferrite microspheres are monodisperse and highly homogeneous. XRD patterns confirm the formation of spinel  $\text{M}^{\text{II}}_x\text{Fe}_{3-x}\text{O}_4$  (M= Mn, Co, Ni) phase, in accord with Raman spectra, which indicate the penetration of the doped atoms into the original lattice structure, resulting in elongated Fe-O bonds. This lattice distortion could lead to the decrease in the grain size, which

might explain the observed smaller sphere dimensions of bimetallic ferrites than pure  $\text{Fe}_3\text{O}_4$ . As expected, increasing the Mn content of  $\text{MnFe}_2\text{O}_4$  ferrite also gives rise to the decrease in the sphere size.



**Figure 1.** SEM images of the as-prepared  $\text{MFe}_2\text{O}_4$  microspheres: (a)  $\text{Fe}_3\text{O}_4$ , (b) Fe-Mn, (c) Fe-Co, and (d) Fe-Ni.

The degree of reduction for the  $\text{MFe}_2\text{O}_4$  ferrites is determined by  $\text{H}_2$  TPR experiments and in-situ XRD as the following order:  $\text{Fe-Ni} > \text{Fe-Co} > \text{Fe}_3\text{O}_4 > \text{Fe-Mn}$ . Additionally, in-situ XRD provides actual information of phase transition and structure evolution during a 5 h  $\text{H}_2$  reduction. While Fe-Co and Fe-Ni are reduced to simple metal alloys, the reduction behavior of Fe-Mn demonstrates a strong dependence on the Mn content. In general, Mn renders the reduction of  $\text{Fe}_3\text{O}_4$  to  $\text{Mn}_x\text{Fe}_{1-x}\text{O}$  rather than  $\text{Fe}^0$ .

**Table 1.** FTO performances of  $\text{MFe}_2\text{O}_4$  microsphere catalysts.

Catalyst	$\text{Fe}_3\text{O}_4$	Fe-5%Mn	Fe-33%Mn	Fe-80%Mn	Fe-Co	Fe-Ni
X(CO), %	6.2	5.6	7.1	3.3	5.3	3.3
S( $\text{CH}_4$ ), C based, %	20.4	20.4	19.2	22.4	27.3	32.8
S( $\text{CO}_2$ ), C based, %	18.4	20.0	24.0	17.8	10.2	8.0
S( $\text{C}_2^-$ - $\text{C}_4^-$ ), C based, %	31.9	42.0	52.6	49.8	21.0	7.5
O/P( $\text{C}_2$ - $\text{C}_4$ )	1.2	1.6	3.6	3.0	0.7	0.2
$\text{C}_{2-4}^-$ STY ( $\text{kg kg}_{\text{cat}}^{-1} \text{h}^{-1}$ )	235.1	273.4	406.9	195.3	132.3	29.4

The catalysts were tested in FTO at 20 bar, 260 °C,  $\text{H}_2/\text{CO} = 1$  and GHSV = 4000  $\text{h}^{-1}$ . As reported in Table 1, Fe-Co and Fe-Ni are more selective towards  $\text{CH}_4$  than lower olefins, although with less  $\text{CO}_2$  produced. This is associated with stronger  $\text{H}_2$  adsorption on the alloy surface, and less iron carbides generated from the alloy – the latter is supported by XRD results of the spent catalysts. Interestingly, Fe-33%Mn is found to exhibit both the highest activity and selectivity for FTO among all ferrites. Further increasing the Mn content has a negative influence on the catalytic activity. The spent catalysts were analyzed by XPS, XRD, Raman and Mossbauer spectroscopy. It is proposed that Mn facilitates CO dissociative adsorption, leading to more deposited carbon that favors the formation of iron carbides. The  $\text{Mn}_x\text{Fe}_{1-x}\text{O}$  phase probably plays an important role in the conversion to  $\varepsilon\text{-Fe}_2\text{C}$ , which is likely to improve the olefin selectivity. However, excessive Mn could possibly encapsulate the iron species and produce the sharp decline in activity. Detailed in-depth discussion of the structure-performance relationships for different  $\text{MFe}_2\text{O}_4$  ferrite microsphere catalysts will be presented.

#### 4. Conclusions

Highly ordered spinel ferrite microspheres were successfully synthesized by implementing a novel solvothermal method as efficient FTO catalysts. Doping of the second metal allows to engineer the structure and performance of bulk iron-based FTO catalyst by changing the amount and type of the doped metal. The insights revealed here by combined use of the state-of-the-art characterization techniques can open a new avenue for controlled synthesis and fine performance regulation of iron-based FTO catalyst.

#### References

- [1] H.M. Torres Galvis, J.H. Bitter, T. Davidian, M. Ruitenbeek, A.I. Dugulan, K.P. de Jong, J. Am. Chem. Soc. 134 (2012) 16207-16215.
- [2] H. Deng, X.L. Li, Q. Peng, X. Wang, J.P. Chen, Y.D. Li, Angew. Chem. Int. Ed. 44 (2005) 2782–2785.
- [3] S. Sun, H. Zeng, D.B. Robinson, S. Raoux, P.M. Rice, S.X. Wang, G. Li, J. Am. Chem. Soc. 126 (2004) 273-279.

#### Keywords

Fischer-Tropsch synthesis; Lower olefins; bulk Fe-based catalyst; bimetallic ferrite microsphere.