Highly Ordered Mesoporous Fe_2O_3-ZrO_2 Bimetal Oxides for an Enhanced CO Hydrogenation Activity to Hydrocarbons

Jae Min Cho,[a] **Jong Wook Bae**[a,*]

[a]*School of Chemical Engineering, Sungkyunkwan University (SKKU), 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea*

**Corresponding author: (Tel.) +82-31-290-7347; (Fax.) +82-31-290-7272; (E-mail.) finejw@skku.edu*

Abstract: Highly ordered mesoporous Fe_2O_3-ZrO_2 mixed bimetal oxides (FeZr) were applied to convert syngas to value-added hydrocarbons through Fischer-Tropsch synthesis reaction. To promote the catalytic activity and structural stability, the irreducible metal oxide of ZrO_2 was incorporated as a structural promoter. At an optimized amount of zirconia (Zr/Fe = 0.25), the activity and structural stability were significantly improved. These enhanced surface properties were mainly due to the formation of the active iron carbide species (χ-Fe_5C_2) with insignificant structural collapses by strong interactions between iron nanoparticles and the ZrO_2 structural promoter, which also suppressed the inactive coke depositions.

Keywords: ordered mesoporous Fe_2O_3-ZrO_2 oxides, structural promoter of ZrO_2, stable χ-Fe_5C_2

1. Introduction

Ordered mesoporous metal oxides have been widely utilized in the field of heterogeneous catalysis due to the large size surface area and controllable pore size as well as the enhanced mass transport rate of the products with less catalyst deactivations [**1,2**]. In order to prevent the catalyst deactivation by the sintering of iron nanoparticles or disintegration of structures during the reaction, ordered mesoporous iron oxide(Fe_2O_3) was synthesized by nano-casting method through an incorporation of irreducible ZrO_2 metal oxide as a structural promoter. The ZrO_2 promoter improved the structural stability significantly by forming the strong interactions and facile active iron carbide phases such as χ-Fe_5C_2 **[3]**.

2. Experimental

Irreducible metal oxide ZrO_2 incorporated mesoporous Fe_2O_3 was synthesized with nano-casting replica method using a hard template of KIT-6 **[4,5]** at a different molar ratio of Zr/Fe from 0 to 1. The prepared catalysts were denoted as FeZr(x), where x represents the molar ratio of Zr/Fe. Catalytic activity test of the mesoporous FeZr catalysts was carried out in fixed bed reactor at the following reaction conditions: T = 300 °C, P = 2.0 MPa, weight hourly space velocity (WHSV) = 8000 L(mixed gas)/kg_{cat}/h and $H_2/N_2/CO$ = 63.0/5.5/31.5. Before the FTS reaction, the catalyst was reduced under a flow of 5%H_2/N_2 at 500 ºC for 12 h. The effluent gases from the reactor were analyzed by using an online gas chromatograph (YoungLin 6500 GC) connected with TCD (SUPELCO-12390-U) and FID (HP-PLOT/Q). To characterize the surface properties of FeZr(x), N_2 sorption, TEM, XRD, H_2-TPR, XPS, XAFS, H_2-TPSR, Raman spectroscopy, and ^{57}Fe Mössbauer spectra were carried out.

3. Results and discussion

The crystallite size of Fe_2O_3 was found to be in the range of 11.8 – 32.4 nm. As the amount of ZrO_2 was increased, the smaller Fe_2O_3 grains were formed due to the well-developed Fe_2O_3-ZrO_2 grain structures. However, the X-ray diffraction (XRD) peaks of ZrO_2 were not clearly observed due to its higher dispersion or intrinsic amorphous characters. As the amount of ZrO_2 metal oxide was increased, the specific surface area was also increased from 110.8 to 209.5 m^2/g due to its structural promoting effect by generating ordered mesoporous structures **[6]**. The catalytic activities on FeZr(x) are summarized in **Table 1**. Compared with the FeZr(0), the catalytic activities were enhanced in all the ZrO_2 incorporated FeZr catalysts. Among them, FeZr(0.3) showed the most stable catalytic activity with a higher C_{5+} and olefin selectivity with the values of 85.6 and 53.6%, respectively. The enhanced FTS activity and stability on the FeZr(0.3) seem to be attributed to an increased degree of reduction and the formation of active and stable iron carbide species instead of a waxy hydrocarbon or coke deposition **[7]**.

Table 1. Physicochemical properties and activities of the mesoporous Fe_2O_3-ZrO_2 catalysts

Catalysts	XRD	N_2 sorption	Activity[a]			Product distribution
	Crystallite size of Fe_2O_3 (nm)	surface area (m^2/g)	CO conv. (C-mol%)	Olefin sel. (C-mol%) [b]	Chain-growth probability (α) [c]	C_1 / C_2-C_4 / C_{5+}
FeZr(0)	32.4	110.8	5.6	72.4	N.A.	7.6 / 14.1 / 78.3
FeZr(0.1)	22.8	127.9	88.3	42.6	0.917	9.6 / 14.1 / 76.3
FeZr(0.3)	18.8	147.6	82.1	53.6	0.928	4.6 / 9.8 / 85.6
FeZr(0.5)	15.9	147.9	77.0	39.6	0.903	9.9 / 14.1 / 76.0
FeZr(1)	11.8	209.5	44.8	37.5	0.918	9.4 / 13.8 / 76.8

[a] FTS reaction was carried out at the following reaction conditions; T = 300 °C, P = 2.0 MPa, WHSV = 8000 L/kg cat/h, and feed gas composition of $H_2/N_2/CO$ = 63.0/5.5/31.5.

[b] Olefin selectivity (C-mol%) was calculated in the C_2 – C_4 light hydrocarbons.

[c] Chain growth probability (α) values were obtained from the Anderson-Schulz-Flory (ASF) distribution in the range of C_{12} - C_{30} hydrocarbons.

As shown in **Figure 1**, the ZrO_2 incorporated FeZr catalyst preserved the ordered mesoporous structures without any significant structural disintegration after FTS reaction. This structural stability was well related with the suppressed aggregation of active components by stronger interactions with ZrO_2 promoters.

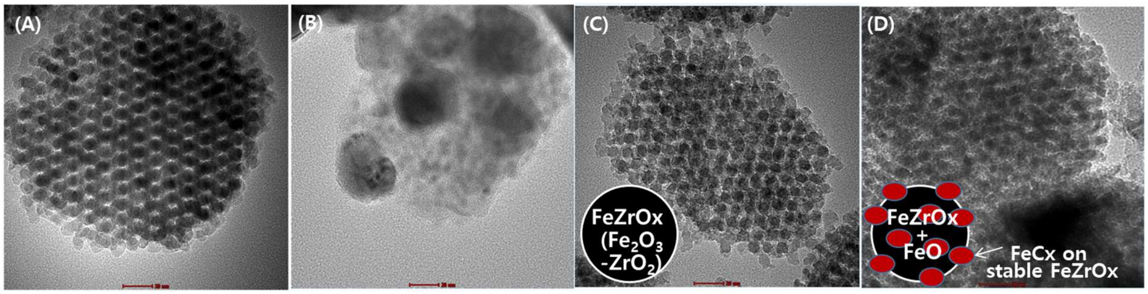

Figure 1. TEM image (20nm scale bar) of (A) fresh FeZr(0), (B) used FeZr(0), (C) fresh FeZr(0.3), and (D) used FeZr(0.3).

The structural disintegrations were also clearly verified by XAFS analysis, in which the co-presence of the larger Fe_2O_3 and metallic Fe phases were observed. In the Mössbauer analysis for the used FeZr catalysts, the content of χ-Fe_5C_2 was found to be higher on the most active FeZr(0.3) due to the stable and smaller iron carbide formation with the help of the strongly interacted FeO-ZrO_2 frameworks.

4. Conclusions

To prevent the structural disintegrations of the mesoporous structures during the reductive FTS reaction conditions, the ordered mesoporous Fe_2O_3 catalysts was synthesized with an incorporation of the irreducible ZrO_2 oxide via nano-casting technique. The stable and enhanced FTS activity on the FeZr(0.3) seem to be attributed to the stabilized mesoporous structures through the stronger interactions between Fe_2O_3 and irreducible ZrO_2 crystallites in the main frameworks of FeZr catalysts by facile formation of the well-known active iron carbide phases such as χ-Fe_5C_2 during FTS reaction.

References

1. P. Shu, J. Ruan, C. Gao, H. Li, S. Che, Micropor. Mesopor. Mater. 123 (2009) 314.
2. J.S. Jung, S.W. Kim, D.J. Moon, Catal. Today. 185 (2012) 168.
3. T. Reidel, H. Schulz, G. Schaub, K.W. Jun, K.W. Hwang, K.W. Lee, Top. Catal. 26 (2003) 41.
4. S. Sun, X. Zhao, M. Yang, L. Wu, Z. Wen, X. Shen, Sci. Rep. 6 (2016) 19564.
5. S. Fei, K. Xia, X. Tian, P. Mei, H. Yan, H. Cheng, Int. J. Hydrogen Energy. 41 (2016) 5652.
6. C.I. Ahn, H.M. Koo, J.M. Jo, H.S. Roh, J.B. Lee, Y.J. Lee, E.J. Jang, J.W. Bae, Appl. Catal. B 180 (2016) 139.
7. S.H. Kang, J.W. Bae, J.Y. Cheon, Y.J. Lee, K.S. Ha, K.W. Jun, D.H. Lee, B.W. Kim, Appl. Catal. B 103 (2011) 169.