**Highly effective MFe2O4 (M=Zn, Mg, Cu and Mn) spinel catalysts for Fischer-Tropsch synthesis**

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**Table S1 Mössbauer spectra fitting parameters of the fresh spinel catalysts**

|  |  |  |  |
| --- | --- | --- | --- |
| Catalysts | Phases | Mössbauer parameters | Area |
|  |  | IS (mm/s) | QS (mm/s) | Hhf (KOe) | (%) |
| ZnFe2O4 | Spm Fea | 0.33 | 0.49 |  | 100 |
| MgFe2O4 | Spm Fe | 0.30 | 0.67 |  | 100 |
| CuFe2O4 | A sitesb | 0.32 | -0.01 | 481 | 51.14 |
| B sites | 0.35 | 0.29 | 423 | 24.22 |
|  |  | 0.39 | 2.54 |  | 8.13 |
|  |  | 0.33 | 0.76 |  | 16.51 |
| MnFe2O4 | Spm Fe | 0.32 | 0.84 |  | 46.98 |
| 0.32 | 0.84 | 520 | 53.02 |

a: superparamagnetic iron ions;

b: A sites – Fe3+ in tetrahedral sites, B sites - Fe3+ in octahedral sites.

**Table S2 Mössbauer spectra fitting parameters of the carbonized and spent catalysts**

|  |  |  |  |
| --- | --- | --- | --- |
| Catalysts | Phases | Mössbauer parameters | Area |
|  |  | IS (mm/s) | QS (mm/s) | Hhf (KOe) | (%) |
| Fe2O3-carbonized | χ-Fe5C2 | 0.27 | 0.09 | 218 | 23.26 |
|  |  | 0.21 | 0.01 | 183 | 24.66 |
|  |  | 0.15 | 0.09 | 102 | 18.17 |
|  | Fe3O4 | 0.74 | -0.03 | 462 | 15.54 |
|  |  | 0.26 | -0.08 | 488 | 5.96 |
|  | Fe3+(spm) | 0.30 | 1.21 |  | 12.41 |
| ZnFe2O4-carbonized | Spm Fe | 0.69 | 0.59 |  | 100 |
| MgFe2O4-carbonized | Spm Fe | 0.47 | 0.77 |  | 100 |
| CuFe2O4-carbonized | χ-Fe5C2 | 0.24 | 0.14 | 220 | 26.46 |
|  |  | 0.19 | -0.02 | 188 | 41.19 |
|  |  | 0.06 | 0.03 | 99 | 26.10 |
|  | Fe2+(spm) | 0.52 | 1.36 |  | 6.25 |
| MnFe2O4-carbonized | χ-Fe5C2 | 0.24 | 0.04 | 217 | 17.47 |
|  |  | 0.18 | -0.05 | 103 | 14.87 |
|  | ε-Fe2C | 0.21 | -0.03 | 180 | 17.52 |
|  | Fe2+(spm) | 1.19 | 0.58 |  | 9.47 |
|  | Fe3+(spm) | 0.31 | 0.67 |  | 40.67 |
| Fe2O3-spent | χ-Fe5C2 | 0.07 | 0.07 | 220 | 10.82 |
|  |  | 0.01 | 0.13 | 103 | 10.66 |
|  | Fe3O4 | 0.29 | -0.01 | 489 | 31.27 |
|  |  | 0.66 | -0.01 | 458 | 47.25 |
| ZnFe2O4-spent | χ-Fe5C2 | 0.00 | 0.15 | 194 | 19.23 |
|  |  | 0.49 | -0.37 | 116 | 12.03 |
|  | Fe3O4 | 0.21 | -0.08 | 462 | 11.80 |
|  |  | 0.22 | 0.01 | 400 | 11.41 |
|  | Fe3+(spm) | 0.36 | 0.42 |  | 45.52 |
| MgFe2O4-spent | χ-Fe5C2 | 0.34 | 0.12 | 212 | 21.58 |
|  | Fe3+(spm) | 0.41 | 0.80 |  | 78.42 |
| CuFe2O4-spent | χ-Fe5C2 | 0.24 | 0.06 | 218 | 18.02 |
|  |  | 0.18 | 0.00 | 182 | 8.49 |
|  | Fe3O4 | 0.29 | 0.00 | 488 | 25.52 |
|  |  | 0.65 | 0.02 | 458 | 32.29 |
|  | Fe3+(spm) | 0.31 | 1.19 |  | 15.68 |
| MnFe2O4-spent | ε-Fe2C | 0.41 | -0.11 | 179 | 3.76 |
|  | χ-Fe5C2 | 0.22 | 0.08 | 217 | 23.95 |
|  |  | 0.11 | 0.08 | 183 | 12.20 |
|  |  | 0.18 | 0.13 | 105 | 18.04 |
|  | Fe3O4 | 0.27 | -0.02 | 485 | 11.83 |
|  |  | 0.62 | 0.03 | 452 | 21.18 |
|  | Fe3+(spm) | 0.28 | 0.94 |  | 9.04 |



Figure S1 Mössbauer spectra of the carbonized catalysts. The blue and green sextets are assigned to A sites and B sites of spinel or Fe3O4, the magenta, olive and violet sextets are assigned to χ-Fe5C2, the cyan sextet is assigned to ε-Fe2C and the yellow and orange doublets are assigned to superparamagnetic Fe2+ and Fe3+.