Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting information

## One-pot catalytic conversion of methanol to C6-C21 hydrocarbons over bi-functional $MFe_2O_4$ (M = Ni, Zn, Mn, Co) catalysts

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## S-1: synthesis conditions of catalysts

**Table S1** The synthesis conditions used for prepared catalysts.

| Sample | $Ni(CH_3COO)_2$ (mmol) | $Zn(CH_3COO)_2$ (mmol) | $Mn(CH_3COO)_2$ (mmol) | $Co(CH_3COO)_2$ (mmol) | $FeCl_3$ (mmol) | $CH_3COONa$ (mmol) | $HOCH_2CH_2OH$ (mL) | $H_2O$ (mL) |
|---|---|---|---|---|---|---|---|---|
| NiO | 2.0 | – | – | – | – | 18 | 40 | 40 |
| ZnO | – | 2.0 | – | – | – | 18 | 40 | 40 |
| $Mn_3O_4$ | – | – | 2.0 | – | – | 18 | 40 | 40 |
| $Co_3O_4$ | – | – | – | 2.0 | – | 18 | 40 | 40 |
| $Fe_3O_4$ | – | – | – | – | 2.0 | 18 | 40 | 40 |
| $NiFe_2O_4$ | 1.0 | – | – | – | 2.0 | 18 | 40 | 40 |
| $ZnFe_2O_4$ | – | 1.0 | – | – | 2.0 | 18 | 40 | 40 |
| $MnFe_2O_4$ | – | – | 1.0 | – | 2.0 | 18 | 40 | 40 |
| $CoFe_2O_4$ | – | – | – | 1.0 | 2.0 | 18 | 40 | 40 |
| $Ni_{0.5}Co_{0.5}Fe_2O_4$ | 0.5 | – | – | 0.5 | 2.0 | 18 | 40 | 40 |
| $Zn_{0.5}Co_{0.5}Fe_2O_4$ | – | 0.5 | – | 0.5 | 2.0 | 18 | 40 | 40 |
| $Mn_{0.5}Co_{0.5}Fe_2O_4$ | – | – | 0.5 | 0.5 | 2.0 | 18 | 40 | 40 |

**S-2：The XPS spectra of $ZnFe_2O_4$ catalyst reduced at 340 $^oC$ with $H_2$**

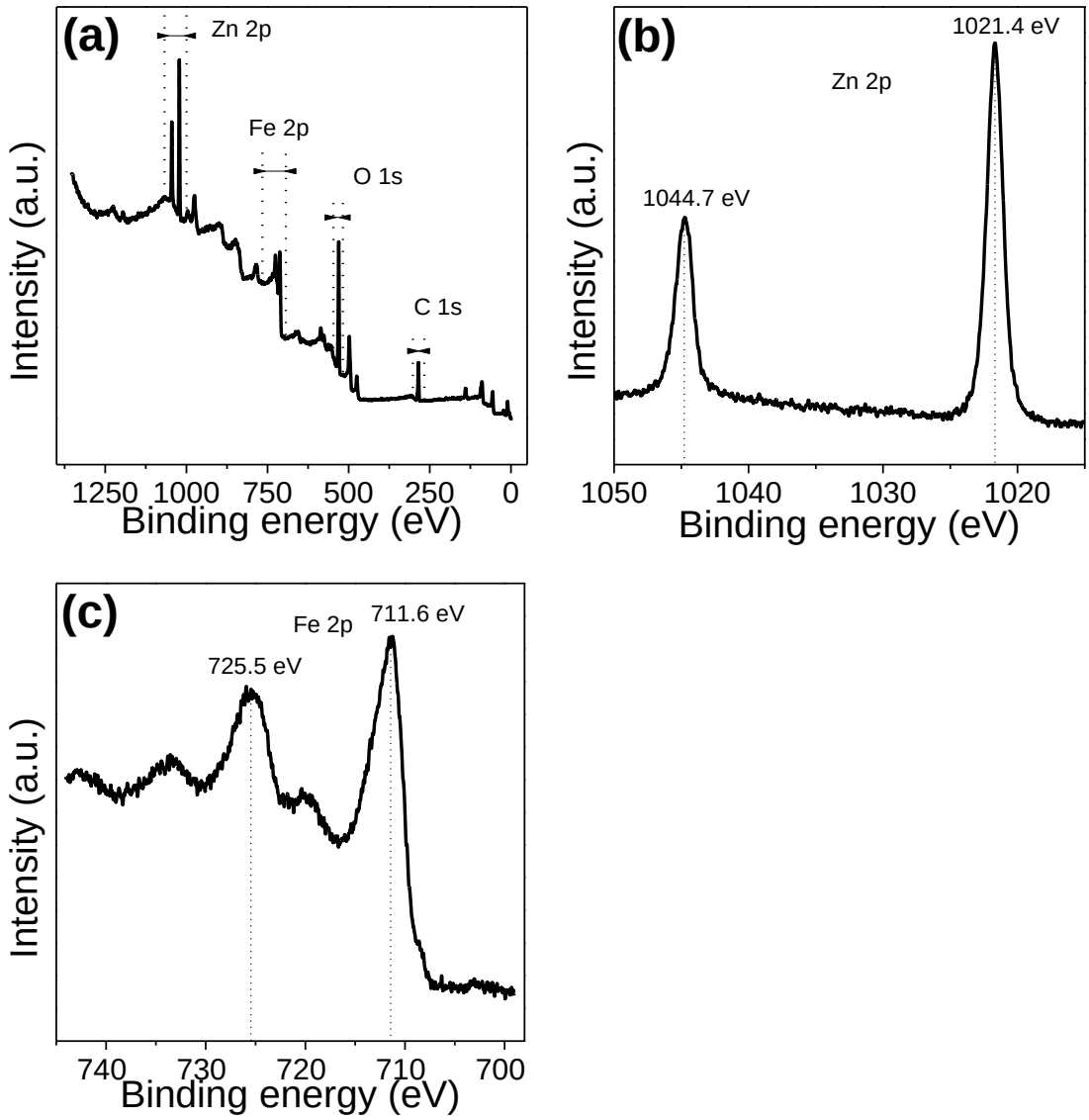


**Fig. S1** XPS spectra of the $ZnFe_2O_4$ catalyst: (a) wide spectrum, (b) Zn2p and (c) Fe 2p spectrum.

## S-3：XRD of used catalyst

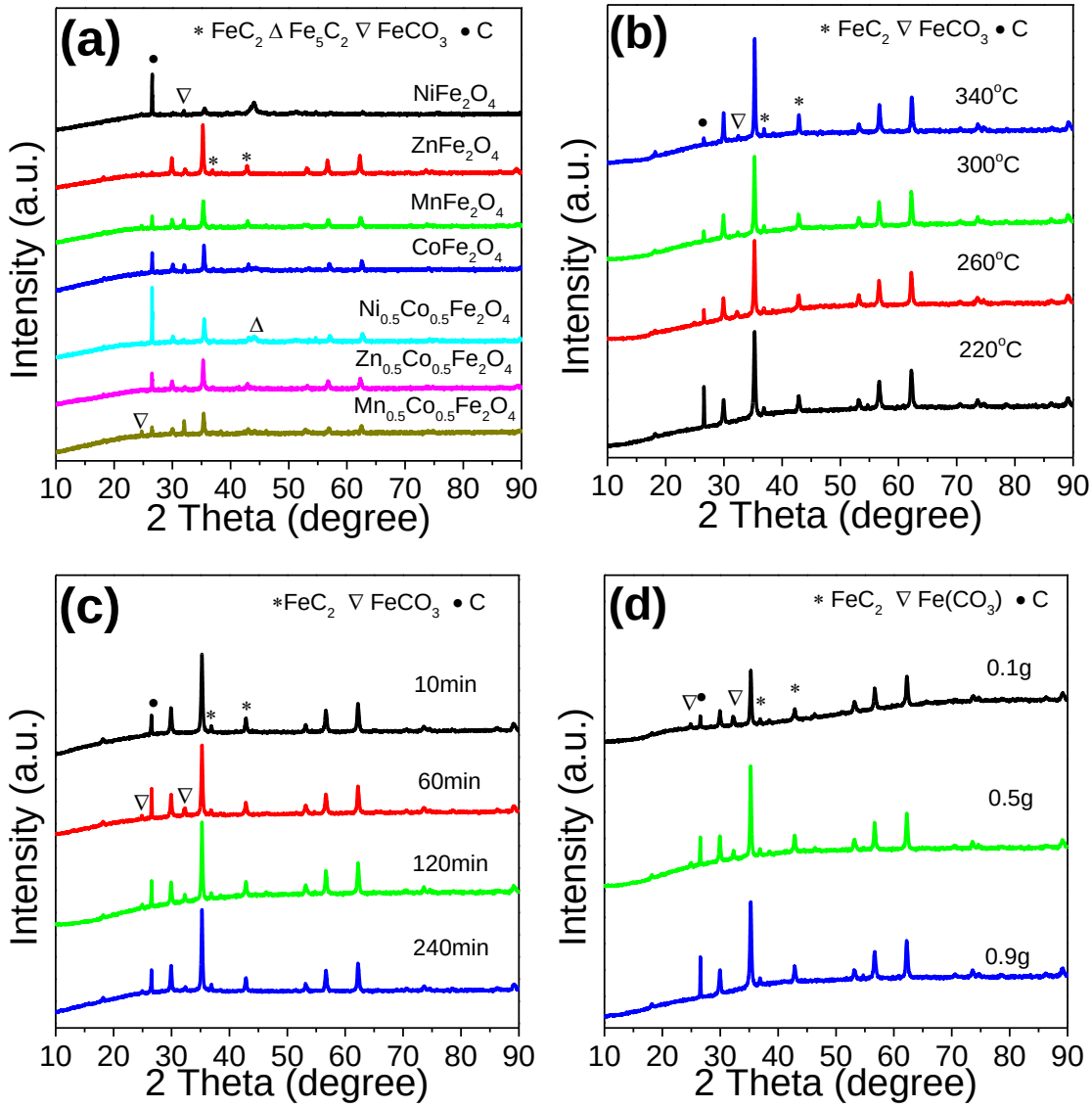


**Fig. S2** XRD patterns of the used catalysts: (a) $MFe_2O_4$ and $M_{0.5}Co_{0.5}Fe_2O_4$ after reaction at 280 °C for 3 h, (b) $ZnFe_2O_4$ reacted at different temperature, (c) different reaction time, and (d) different catalyst amount.

## S-4：SEM and elemental mapping characterization

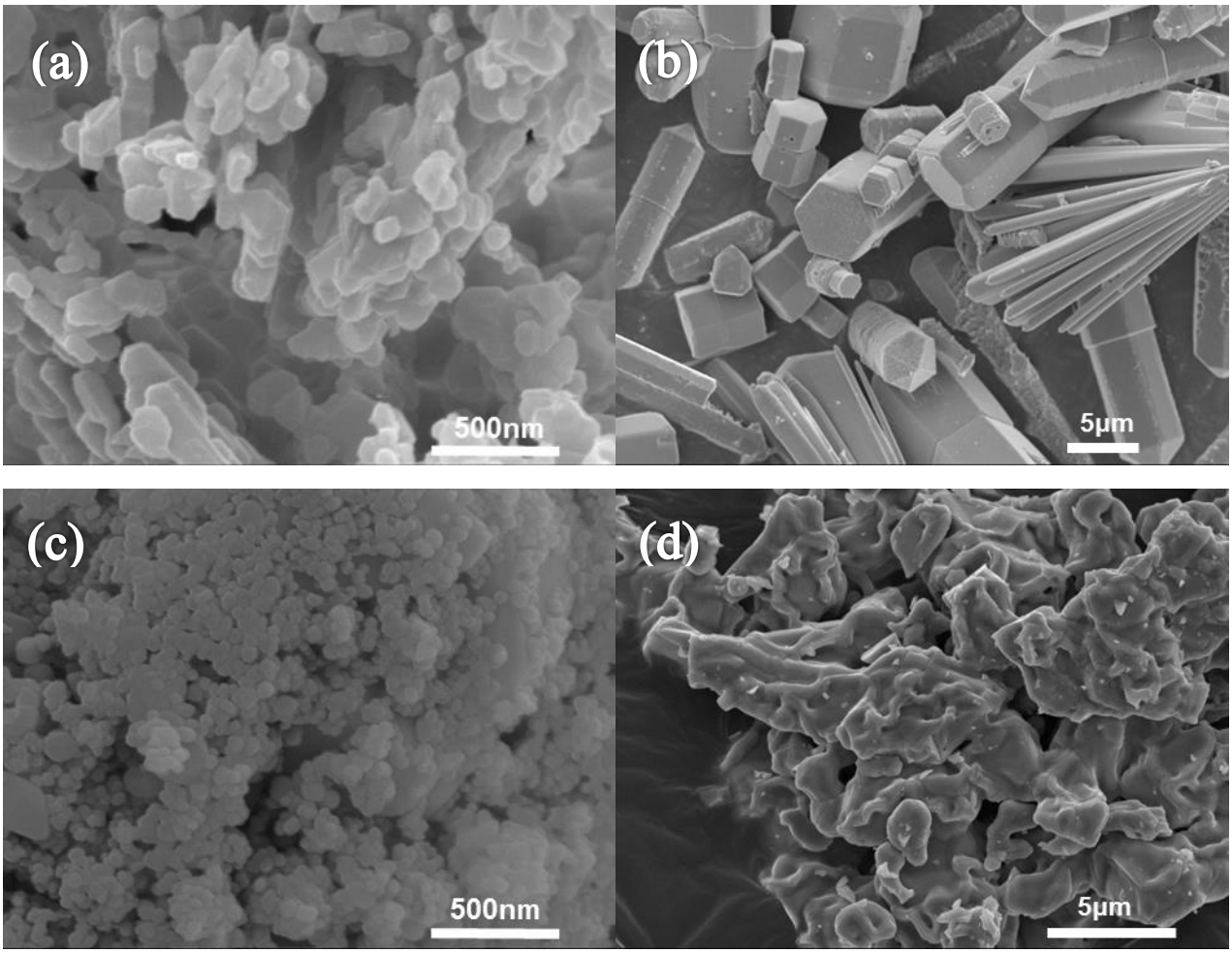


**Fig. S3** SEM images of the catalysts: (a) NiO, (b) ZnO, (c) $Mn_3O_4$, and (d) $Co_3O_4$.

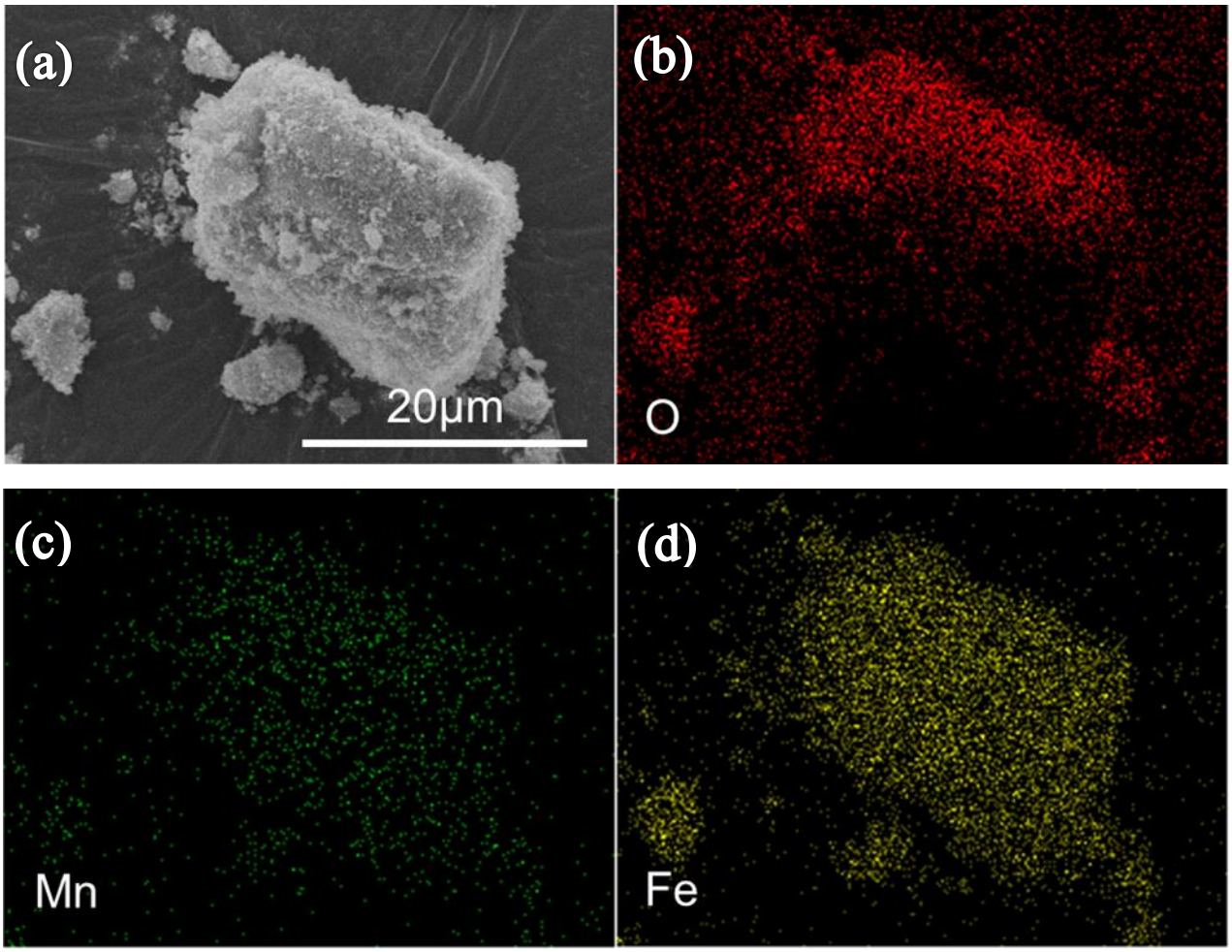


**Fig. S4** SEM image of $MnFe_2O_4$ (a) and the corresponding elemental mapping images of O (b), Mn (c), and Fe (d).

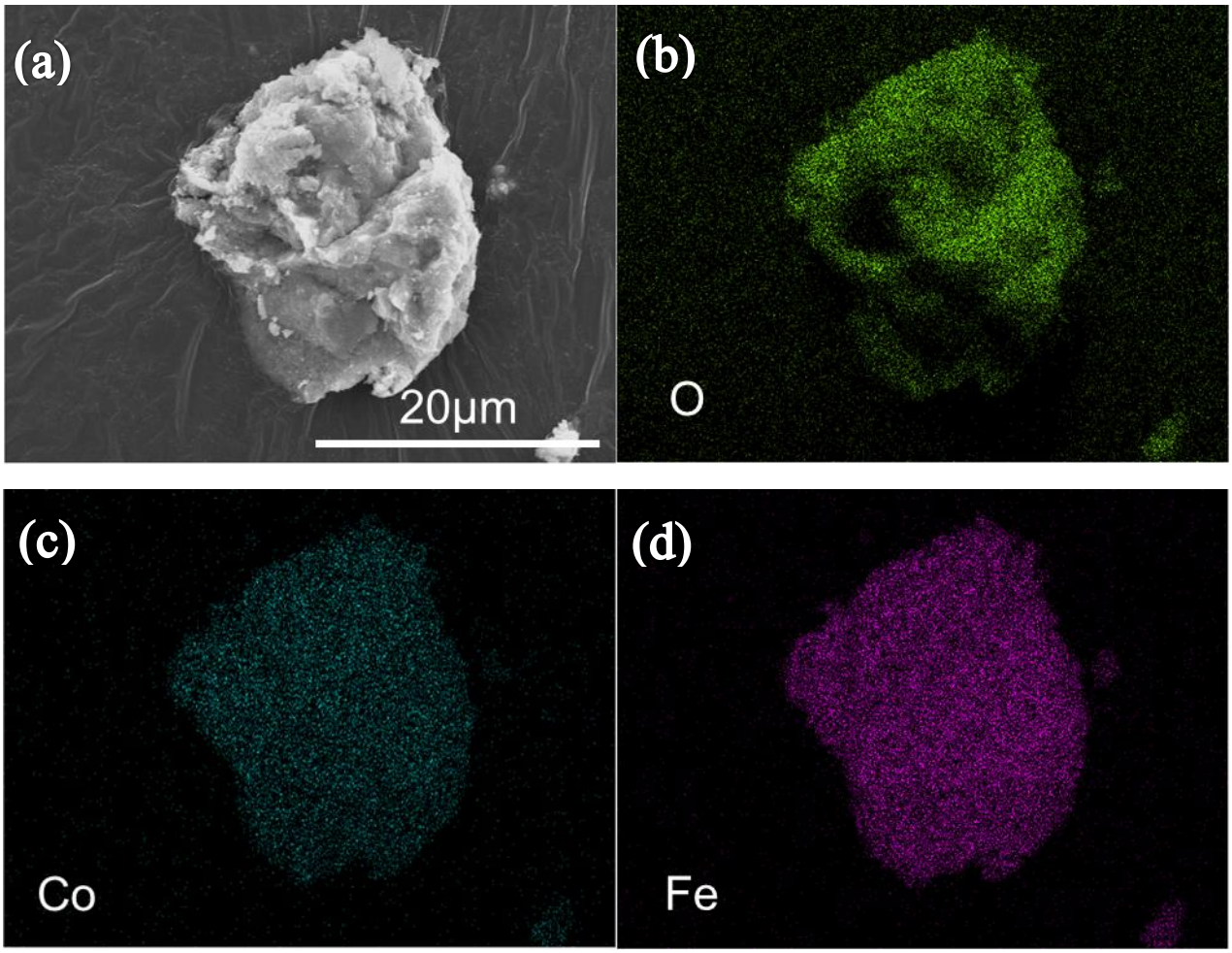


**Fig. S5** SEM image of $CoFe_2O_4$ (a) and the corresponding elemental mapping images of O (b), Mn (c), and Fe (d).

## S-5: The composition of C6-C21 hydrocarbon products under different conditions

**Table S2** The composition of C6-C21 hydrocarbon in liquid products over $MFe_2O_4$ catalysts. (peak area %)

| Entry | C6-C21 hydrocarbon | Catalyst | | | |
|---|---|---|---|---|---|
| | | $NiFe_2O_4$ | $ZnFe_2O_4$ | $MnFe_2O_4$ | $CoFe_2O_4$ |
| **1** | 2,4-dimethyl-Pentane | N/A | N/A | 3.55 | N/A |
| **2** | 1,3-dimethyl-Cyclopentane | 0.87 | N/A | N/A | N/A |
| **3** | ethyl-Cyclopentane | N/A | N/A | N/A | 0.95 |
| **4** | 2-methyl-Hexane | 1.97 | 1.95 | N/A | 4.52 |
| **5** | 3-methyl-Hexane | 1.81 | 2.30 | N/A | 4.95 |
| **6** | 3-Methyl-2-hexene | N/A | 0.97 | N/A | N/A |
| **7** | 2,4-dimethyl-Hexane | 2.11 | 3.14 | N/A | N/A |
| **8** | 1-Heptene | N/A | N/A | 10.69 | N/A |
| **9** | Heptane | 5.65 | 14.76 | 7.88 | 21.21 |
| **10** | 2-methyl-Heptane | 1.24 | 1.02 | N/A | N/A |
| **11** | 3-methyl-Heptane | N/A | N/A | N/A | 3.92 |
| **12** | 4-methyl-Heptane | N/A | N/A | N/A | N/A |
| **13** | 2-Heptene | N/A | 1.20 | 3.73 | N/A |
| **14** | 3-Heptene | N/A | N/A | N/A | N/A |
| **15** | p-Xylene | N/A | N/A | N/A | 1.01 |
| **16** | Ethyl benzene | N/A | N/A | N/A | 1.02 |
| **17** | 1-Octene | N/A | N/A | 9.58 | N/A |
| **18** | Octane | 4.95 | 15.56 | 6.62 | 16.23 |
| **19** | 2-Octene | N/A | N/A | 2.53 | N/A |
| **20** | 2-methyl-Octane | N/A | 2.62 | N/A | 3.76 |
| **21** | 3-methyl-Octane | N/A | 1.48 | N/A | 2.02 |
| **22** | 4-methyl-Octane | N/A | N/A | N/A | N/A |
| **23** | 1-methyl-Indan | N/A | N/A | N/A | 0.54 |
| **24** | 1-Nonene | N/A | N/A | 6.96 | N/A |
| **25** | Nonane | 4.01 | 13.16 | 5.6 | 10.23 |
| **26** | cis-2-Nonene | N/A | N/A | 4.47 | N/A |
| **27** | Decane | 4.99 | 10.09 | N/A | 5.91 |
| **28** | 2-methyl-Decane | N/A | N/A | N/A | 0.65 |
| **29** | 3-methyl-Decane | N/A | N/A | N/A | N/A |
| **30** | 2-methyl-Nonane | N/A | 0.95 | N/A | 1.15 |
| **31** | 3-methyl-Nonane | N/A | 1.54 | N/A | 1.57 |
| **32** | 4-methyl-Nonane | N/A | 1.04 | N/A | 2.26 |
| **33** | 5-(2-methylpropyl)-Nonane | N/A | 0.93 | N/A | 0.87 |
| **34** | 1-Decene | N/A | N/A | 3.96 | N/A |
| **35** | Undecane | N/A | N/A | 4.21 | 3.08 |

| | | | | | |
|---|---|---|---|---|---|
| **36** | 1-ethyl-2-heptyl-Cyclopropane | N/A | N/A | 2.33 | N/A |
| **37** | 1-Decene | N/A | N/A | 1.61 | N/A |
| **38** | 1-Undecene | N/A | N/A | 2.28 | N/A |
| **39** | Undecane | N/A | N/A | 3.59 | N/A |
| **40** | 1-Undecene | N/A | N/A | 1.74 | N/A |
| **41** | 1-Undecene | N/A | N/A | 1.13 | N/A |
| **42** | 1-Dodecene | N/A | N/A | 1.41 | N/A |
| **43** | Dodecane | 6.37 | 12.18 | 3.53 | 1.76 |
| **44** | nonyl-Cyclopropane | N/A | N/A | 1.46 | N/A |
| **45** | 3-Tetradecene | N/A | N/A | 0.96 | N/A |
| **46** | Tridecane | 3.71 | 3.66 | 2.06 | 0.90 |
| **47** | Tetradecane | 2.15 | 2.57 | 1.22 | N/A |
| **48** | Hexadecane | 3.80 | 2.88 | N/A | N/A |
| **49** | (2,3-dimethyldecyl)-Benzene | N/A | N/A | N/A | 0.81 |
| | **Total peak area %** | **43.63** | **94** | **93.1** | **89.32** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available.

**Table S3** The composition of C6-C21 hydrocarbon in liquid products over $M_{0.5}Co_{0.5}Fe_2O_4$ catalysts.

(peak area %)

| Entry | C6-C21 hydrocarbon | Catalyst | | |
|---|---|---|---|---|
| | | $Ni_{0.5}Co_{0.5}Fe_2O_4$ | $Zn_{0.5}Co_{0.5}Fe_2O_4$ | $Mn_{0.5}Co_{0.5}Fe_2O_4$ |
| **1** | 2,4-dimethyl-Pentane | N/A | N/A | 3.41 |
| **2** | 2-methyl-Hexane | 2.43 | N/A | N/A |
| **3** | 3-methyl-Hexane | 2.04 | 2.49 | 3.4 |
| **4** | Heptane | 10.1 | 14.61 | 17.29 |
| **5** | 2-Heptene | N/A | 1.95 | N/A |
| **6** | 3-methyl-Heptane | 2.06 | 4.19 | 3.17 |
| **7** | Toluene | N/A | N/A | N/A |
| **8** | 2,4-dimethyl-Hexane | N/A | 15.62 | 14.42 |
| **9** | Ethyl benzene | N/A | N/A | 1.23 |
| **10** | 5-methyl-Undecane | N/A | N/A | 3.16 |
| **11** | Octane | 12.64 | N/A | N/A |
| **12** | 2-Octene | N/A | 0.97 | N/A |
| **13** | 2-methyl-Octane | 2.71 | N/A | N/A |
| **14** | 3-methyl- Octane | 1.79 | 2.36 | 2.15 |
| **15** | 4-methyl- Octane | N/A | 2.38 | N/A |
| **16** | 2,4,6-trimethyl-Octane | N/A | N/A | 5.95 |
| **17** | o-Xylene | N/A | N/A | N/A |
| **18** | p-Xylene | 0.88 | N/A | N/A |
| **19** | Nonane | 12.09 | 11.56 | 10.26 |
| **20** | 4-methyl-Nonane | 1.55 | N/A | 1.99 |
| **21** | 2-methyl-Nonane | 1.12 | N/A | 0.99 |
| **22** | 3-methyl-Nonane | 1.42 | 0.98 | 1.28 |
| **23** | 2,5-dimethyl-Nonane | 0.57 | N/A | N/A |
| **24** | 5-(2-methylpropyl)-Nonane | 0.44 | N/A | N/A |
| **25** | Decane | 8.76 | 7.7 | N/A |
| **26** | 2-methyl-Decane | 0.76 | N/A | 1.17 |
| **27** | 3-methyl-Decane | 0.68 | N/A | 1.04 |
| **28** | 4-methyl-Decane | 0.56 | N/A | N/A |
| **29** | Indane | N/A | N/A | N/A |
| **30** | 1,3-dimethyl-Benzene | 0.68 | N/A | 0.96 |
| **31** | (2,3-dimethyldecyl)- Benzene | N/A | N/A | N/A |
| **32** | 2-methyl-Decane | N/A | N/A | N/A |
| **33** | (2-methyloctyl)-Benzene | 3.63 | N/A | N/A |
| **34** | 3-methyl-Decane | N/A | N/A | N/A |
| **35** | 1-methyl-2-(2-propenyl)-Benzene | N/A | N/A | N/A |
| **36** | 1-methyl-Indan | N/A | N/A | N/A |
| **37** | Undecane | 5.35 | 5.06 | 3.02 |
| **38** | 4-ethyl-Octane | N/A | N/A | N/A |

| | | | | |
|---|---|---|---|---|
| **39** | Dodecane | 2.35 | 5.28 | N/A |
| **40** | Tridecane | 1.67 | 1.95 | N/A |
| **41** | Tetradecane | 1.02 | N/A | N/A |
| **42** | Hexadecane | N/A | 1.20 | N/A |
| | **Total peak area %** | **77.3** | **78.3** | **76.38** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available.

**Table S4** Effect of reaction temperature on the composition of C6-C21 hydrocarbon in liquid products over $ZnFe_2O_4$ catalyst. (peak area %)

| Entry | C6-C21 hydrocarbon | Reaction temperature | | | | | |
|---|---|---|---|---|---|---|---|
| | | 240 ℃ | 260 ℃ | 280 ℃ | 300 ℃ | 320 ℃ | 340 ℃ |
| 1 | 2-methyl-Hexane | N/A | 2.44 | 1.95 | 2.84 | N/A | N/A |
| 2 | 3-methyl-Hexane | N/A | 2.21 | 2.30 | 3.22 | 3.181 | 2.98 |
| 3 | 3-Methyl-2-hexene | N/A | N/A | 0.97 | 2.47 | 3.45 | 2.79 |
| 4 | 2,4,6-trimethyl-Heptane | N/A | N/A | N/A | N/A | N/A | 3.61 |
| 5 | Octane | 2.20 | N/A | N/A | N/A | N/A | N/A |
| 6 | 1-Heptene | 14.45 | 3.95 | N/A | N/A | N/A | N/A |
| 7 | Heptane | 3.03 | 13.79 | 14.76 | 18.16 | 17.25 | 14.85 |
| 8 | 2-Heptene | N/A | 5.00 | 1.20 | 3.57 | N/A | 3.16 |
| 9 | 3-Heptene | N/A | 2.76 | N/A | 1.71 | 6.43 | 1.50 |
| 10 | 2-methyl-Heptane | N/A | N/A | 3.02 | N/A | N/A | 1.73 |
| 11 | 3-methyl- Heptane | N/A | N/A | N/A | N/A | N/A | 3.06 |
| 12 | 2,4-dimethyl-Hexane | N/A | N/A | 3.14 | 3.25 | N/A | N/A |
| 13 | 1-Octene | 10.41 | 1.71 | N/A | N/A | N/A | N/A |
| 14 | Octane | 2.97 | 12.97 | 15.56 | 16.36 | 15.53 | 14.53 |
| 15 | 2-Octene | N/A | 3.39 | N/A | 2.03 | N/A | 1.81 |
| 16 | 3-Octene | N/A | 2.10 | N/A | N/A | 3.82 | N/A |
| 17 | 2-methyl-Octane | N/A | N/A | 2.62 | N/A | N/A | N/A |
| 18 | 4-methyl-Octane | N/A | 1.97 | N/A | 3.00 | 3.11 | 3.66 |
| 19 | 3-methyl-Octane | N/A | 1.41 | 1.48 | 1.69 | 1.68 | 1.86 |
| 20 | 2,6,6-trimethyl-Octane | N/A | N/A | N/A | N/A | N/A | 1.33 |
| 21 | 1-Nonene | 9.13 | 1.39 | N/A | N/A | 0.83 | N/A |
| 22 | 2-Nonene | N/A | 4.16 | N/A | 1.42 | 1.76 | 1.58 |
| 23 | Nonane | 2.91 | 10.61 | 13.16 | 12.04 | 11.41 | 11.84 |
| 24 | 2-methyl-Nonane | N/A | N/A | 0.95 | N/A | N/A | 1.27 |
| 25 | 3-methyl- Nonane | N/A | N/A | 1.54 | 1.22 | 1.19 | 1.47 |
| 26 | 4-methyl- Nonane | N/A | N/A | 1.04 | N/A | N/A | 1.59 |
| 27 | 5-(2-methylpropyl)- Nonane | N/A | N/A | 0.93 | 0.95 | 0.92 | 1.18 |
| 28 | 1-Decene | 6.96 | 1.82 | N/A | N/A | N/A | N/A |
| 29 | Decane | 2.76 | 7.50 | 10.09 | 7.51 | 7.99 | 7.29 |
| 30 | trans-3-Decene | N/A | N/A | N/A | 0.79 | 1.01 | N/A |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 31 | 5-methyl-Decane | N/A | N/A | N/A | N/A | 3.79 | N/A |
| 32 | 1-Undecene | 5.18 | N/A | N/A | N/A | N/A | N/A |
| 33 | Undecane | 2.55 | 5.67 | N/A | 5.14 | 4.41 | 3.73 |
| 34 | Dodecane | 2.27 | 4.34 | 12.14 | 3.30 | 2.78 | 2.90 |
| 35 | Tridecane | 3.5 | 3.33 | 3.66 | N/A | 1.68 | 0.66 |
| 36 | 1-Tridecene | 6.54 | N/A | N/A | N/A | N/A | N/A |
| 37 | 4,6-dimethyl-Dodecane | N/A | N/A | N/A | 2.07 | N/A | N/A |
| 38 | Tetradecane | 3.66 | 2.70 | 3.66 | 1.37 | 1.09 | N/A |
| 39 | 1-Pentadecene | 1.68 | N/A | N/A | N/A | N/A | N/A |
| 40 | Pentadecane | 3.63 | 1.96 | N/A | N/A | N/A | N/A |
| 41 | Hexadecane | 2.96 | 1.30 | 2.88 | 0.82 | N/A | N/A |
| 42 | Heptadecane | 3.62 | N/A | N/A | N/A | N/A | N/A |
| 43 | 3-Octadecene | 2.30 | N/A | N/A | N/A | N/A | N/A |
| 44 | Eicosane | 1.41 | N/A | N/A | N/A | N/A | N/A |
| 45 | Heneicosane | 4.90 | N/A | N/A | N/A | N/A | N/A |
| | **Total peak area %** | **99.02** | **98.48** | **97.05** | **94.93** | **89.521** | **90.38** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available.

**Table S5** Effect of reaction time on the composition of C6-C21 hydrocarbon in liquid products over $ZnFe_2O_4$ catalyst. (peak area %)

| Entry | C6-C21 hydrocarbon | Reaction time | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10 min | 30 min | 60 min | 120 min | 180 min | 240 min |
| 1 | 2,4-dimethyl-Pentane | N/A | N/A | 1.88 | N/A | N/A | N/A |
| 2 | 1-Heptene | 10.47 | 6.33 | 4.00 | N/A | N/A | N/A |
| 3 | Heptane | 4.91 | 11.34 | 13.66 | 13.39 | 18.16 | 16.60 |
| 4 | 2-Heptene | N/A | N/A | N/A | N/A | 3.57 | N/A |
| 5 | 3-Heptene | N/A | 5.58 | 7.05 | 6.75 | 1.71 | 5.62 |
| 6 | 2-methyl-Hexane | N/A | 1.62 | N/A | 2.86 | 2.84 | 2.72 |
| 7 | 3-methyl-Hexane | N/A | 1.74 | 2.22 | 2.41 | 3.22 | 2.98 |
| 8 | 2,4-dimethyl-Hexane | N/A | N/A | N/A | 3.26 | 3.25 | 3.09 |
| 9 | 3-Methyl-2-hexene | N/A | N/A | N/A | N/A | 2.47 | 2.65 |
| 10 | 1-Octene | 8.87 | 4.30 | 2.22 | N/A | N/A | N/A |
| 11 | 2-Octene | N/A | N/A | N/A | N/A | 2.03 | N/A |
| 12 | Octane | 5.14 | 11.18 | 13.32 | 13.25 | 16.36 | 15.48 |
| 13 | 3-methyl-Octane | N/A | N/A | 1.42 | 1.43 | 1.69 | 1.60 |
| 14 | 4-methyl-Octane | N/A | N/A | N/A | 2.44 | 3.00 | 2.91 |
| 15 | 5-ethyl-2-methyl-Octane | N/A | N/A | N/A | 5.57 | N/A | N/A |
| 16 | 3-Octene | N/A | 4.69 | 5.05 | 5.01 | N/A | 3.48 |
| 17 | 1-Nonene | 7.27 | 4.72 | 3.02 | 7.87 | N/A | N/A |
| 18 | Nonane | 4.91 | 9.44 | 10.81 | 10.62 | 12.04 | 11.3 |
| 19 | 2-Nonene | N/A | 2.55 | 2.59 | 2.45 | 1.42 | 1.57 |
| 20 | 3-methyl-Nonane | N/A | N/A | N/A | N/A | 1.22 | N/A |
| 21 | 5-(2-methylpropyl)-Nonane | N/A | N/A | N/A | N/A | 0.95 | N/A |
| 22 | 1-Decene | 5.34 | 1.55 | N/A | N/A | N/A | N/A |
| 23 | Decane | 4.64 | 7.40 | 7.82 | 8.14 | 7.51 | 8.03 |
| 24 | 1-Decene | 1.02 | 2.02 | N/A | 1.63 | N/A | N/A |
| 25 | trans-3-Decene | N/A | N/A | N/A | N/A | 0.79 | 0.96 |
| 26 | 1-Undecene | 4.34 | 1.47 | N/A | N/A | N/A | N/A |
| 27 | Undecane | 4.78 | 6.47 | 6.10 | N/A | 5.14 | 4.76 |
| 28 | 3-Dodecene | N/A | N/A | 1.86 | N/A | N/A | N/A |
| 29 | 1-Dodecene | 3.27 | N/A | N/A | N/A | N/A | N/A |
| 30 | Dodecane | 4.59 | 5.10 | 4.53 | 4.97 | 3.30 | 3.12 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 31 | Tridecane | 4.09 | 3.77 | 3.30 | 2.21 | N/A | 1.97 |
| 32 | 1-Tridecene | 2.34 | N/A | N/A | N/A | N/A | N/A |
| 33 | 4,6-dimethyl-Dodecane | N/A | N/A | N/A | N/A | 2.07 | N/A |
| 34 | 3-Tetradecene | 1.03 | N/A | N/A | N/A | N/A | N/A |
| 35 | 7-methyl-Tridecane | N/A | N/A | N/A | N/A | N/A | 1.11 |
| 36 | 3-Octadecene | 1.75 | N/A | N/A | N/A | N/A | N/A |
| 37 | Tetradecane | 3.91 | 3.33 | 2.62 | 1.82 | 1.37 | 1.31 |
| 38 | 1-Pentadecene | 1.25 | N/A | N/A | N/A | N/A | N/A |
| 39 | Hexadecane | 7.46 | 4.16 | 3.77 | N/A | 0.82 | N/A |
| 40 | Heptadecane | 3.27 | 1.24 | 1.22 | N/A | N/A | N/A |
| 41 | Octadecane | 2.20 | N/A | N/A | N/A | N/A | N/A |
| 42 | Nonadecane | 1.81 | N/A | N/A | N/A | N/A | N/A |
| 43 | Heneicosane | 1.34 | N/A | N/A | N/A | N/A | N/A |
| | **Total peak area %** | **100** | **100** | **98.46** | **96.08** | **94.93** | **91.26** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available.

**Table S6** Effect of catalyst amount on the composition of C6-C21 hydrocarbon in liquid products over $ZnFe_2O_4$ catalyst. (peak area %)

| Entry | C6-C21 hydrocarbon | catalyst amount | | | |
|---|---|---|---|---|---|
| | | **0.1 g** | **0.3 g** | **0.5 g** | **0.9 g** |
| 1 | 3-ethyl-1-Pentene | N/A | 1.38 | N/A | N/A |
| 2 | 2-methyl-Hexane | 2.57 | 3.19 | 2.86 | 1.87 |
| 3 | 3-methyl-Hexane | 3.36 | 3.44 | 2.41 | 2.46 |
| 4 | 2,4-dimethyl-Hexane | N/A | N/A | 3.26 | 3.20 |
| 5 | Heptane | 17.32 | 19.13 | 13.39 | 14.48 |
| 6 | 2-Heptene | 2.4 | N/A | N/A | 1.7 |
| 7 | 3-Heptene | N/A | 1.94 | 6.75 | N/A |
| 8 | 2-methyl-Heptane | 2.21 | 2.32 | N/A | N/A |
| 9 | 4-methyl-Heptane | 1.13 | 1.12 | N/A | N/A |
| 10 | 3-methyl-Heptane | 3.13 | 2.96 | N/A | N/A |
| 11 | Octane | 16.2 | 16.8 | 13.25 | 15.44 |
| 12 | 2-Octene | 0.81 | N/A | N/A | 1.00 |
| 13 | 3-Octene | N/A | 0.92 | 5.01 | N/A |
| 14 | 4-methyl-Octane | 3.23 | 3.15 | 2.44 | 3.18 |
| 15 | 3-methyl-Octane | 1.68 | 1.60 | 1.43 | 1.71 |
| 16 | Nonane | 12.44 | 12.12 | 10.62 | 12.89 |
| 17 | 5-ethyl-2-methyl-Octane | N/A | 5.59 | 5.57 | N/A |
| 18 | 1-Nonene | N/A | 1.19 | 7.87 | N/A |
| 19 | cis-2-Nonene | N/A | N/A | 2.45 | N/A |
| 20 | 4-methyl-Nonane | 1.22 | 1.09 | N/A | N/A |
| 21 | 2-methyl- Nonane | 1.06 | 1.02 | N/A | 1.02 |
| 22 | 3-methyl-Nonane | 1.72 | 1.54 | N/A | 1.44 |
| 23 | Decane | 8.66 | 8.16 | 8.14 | 9.5 |
| 24 | 1-Decene | N/A | N/A | 1.63 | N/A |
| 25 | 4-methyl- Decane | 0.80 | N/A | N/A | N/A |
| 26 | 2-methyl-Decane | 0.78 | N/A | N/A | 0.97 |
| 27 | 5-(2-methylpropyl)-Nonane | 1.03 | N/A | N/A | 1.18 |
| 28 | Undecane | 6.15 | N/A | N/A | 7.16 |
| 29 | Dodecane | 4.03 | 3.64 | 4.97 | 4.93 |
| 30 | 4,6-dimethyl-Dodecane | N/A | N/A | N/A | 3.47 |
| 31 | Tridecane | 2.89 | N/A | 2.21 | N/A |
| 32 | Tetradecane | 1.91 | 1.71 | 1.82 | 2.21 |
| 33 | Hexadecane | 1.20 | 3.57 | N/A | 1.33 |
| | **Total peak area %** | **97.93** | **97.58** | **96.08** | **91.14** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available

**Table S7** The composition of C6-C21 hydrocarbon in liquid products over $ZnFe_2O_4$ catalyst for 4 runs reactions. (peak area %)

| Entry | C6-C21 hydrocarbon | Four circles | | | |
|---|---|---|---|---|---|
| | | Run1 | Run2 | Run3 | Run4 |
| 1 | 2,3,4-trimethyl-Pentane | N/A | 1.33 | 1.38 | N/A |
| 2 | 2-methyl-Hexane | 2.86 | 3.14 | 4.12 | 4.28 |
| 3 | 3-methyl- Hexane | 2.41 | 3.68 | 4.69 | 4.65 |
| 4 | 1-Nonene | 5.11 | N/A | N/A | N/A |
| 5 | Heptane | 13.39 | 17.69 | 19.24 | 19.15 |
| 6 | 2-Heptene | N/A | 1.84 | 1.21 | 1.30 |
| 7 | 3-Heptene | 4.25 | N/A | N/A | N/A |
| 8 | 3-Heptene | 2.50 | N/A | N/A | N/A |
| 9 | 2-methyl-Heptane | N/A | 3.42 | 3.47 | 3.94 |
| 10 | 3-methyl-Heptane | N/A | 4.15 | 4.08 | 4.28 |
| 11 | 4-methyl-Heptane | N/A | N/A | N/A | 1.34 |
| 12 | 2,5,5-trimethyl-Heptane | N/A | 0.81 | 0.80 | 0.78 |
| 13 | 3-Methyl-2-hexene | N/A | N/A | N/A | 2.48 |
| 14 | 2,4-dimethyl-Hexane | 3.26 | N/A | N/A | N/A |
| 15 | p-Xylene | N/A | N/A | N/A | 0.63 |
| 16 | Octane | 13.25 | 17.21 | 16.56 | 16.82 |
| 17 | 3-Octene | 5.01 | N/A | N/A | N/A |
| 18 | 2-methyl-Octane | N/A | 4.13 | 4.12 | 4.31 |
| 19 | 4-methyl-Octane | 2.44 | N/A | N/A | N/A |
| 20 | 3-methyl- Octane | 1.43 | 2.26 | 2.19 | 2.32 |
| 21 | 1-Nonene | 1.44 | N/A | N/A | N/A |
| 22 | Nonane | 10.62 | 12.58 | 11.65 | 11.65 |
| 23 | 3-methyl-Nonane | N/A | 2.00 | 1.93 | 2.01 |
| 24 | 4-methyl-Nonane | N/A | 1.57 | 1.53 | 1.52 |
| 25 | 5-methyl-Nonane | N/A | 0.74 | 0.71 | 0.78 |
| 26 | cis-2-Nonene | 2.45 | N/A | N/A | N/A |
| 27 | 1-Nonene | 1.32 | N/A | N/A | N/A |
| 28 | 2,5-dimethyl-Nonane | N/A | 0.80 | 0.83 | 0.82 |
| 29 | 5-(2-methylpropyl)-Nonane | N/A | 1.09 | 1.09 | 1.09 |
| 30 | Decane | 8.14 | 7.74 | 7.24 | 6.88 |
| 31 | 1-Decene | 1.63 | N/A | N/A | N/A |
| 32 | 2-methyl-Decane | N/A | 0.84 | 0.87 | 0.84 |
| 33 | 3,6-dimethyl-Decane | N/A | N/A | 0.64 | N/A |
| 34 | 5-ethyl-2-methyl-Octane | 5.57 | N/A | N/A | N/A |
| 35 | Undecane | N/A | 4.47 | 4.36 | 3.84 |
| 36 | Dodecane | 4.97 | 2.36 | 2.4 | 3.36 |
| 37 | Tridecane | 2.21 | 2.54 | 2.61 | 0.93 |
| 38 | Tetradecane | 1.82 | N/A | N/A | N/A |
| | **Total peak area %** | **96.08** | **96.39** | **97.72** | **100** |

Note: Data in this table represent the percentage of peak area detected by GC/MS. “Total peak area %” represents the total peak area percentage of C6-C21 hydrocarbons among the detected products. “N/A” represents not available.

## S-6: The synthesis and characterization of supported $ZnFe_2O_4$

We also choose different supports to load the $ZnFe_2O_4$ to test catalytic activity of selective conversion of methanol to C6-C21 hydrocarbons. In this paper, α-$Al_2O_3$, γ-$Al_2O_3$, CB (carbon black), GCB (graphitized carbon black) and CNT (carbon nano tube) were used as supports.

### Catalysts Synthesis

In a typical synthesis, $Zn(CH_3COO)_2$•$4H_2O$ (3.0 mmol), $FeCl_3$•$6H_2O$ (6.0 mmol), and $CH_3COONa$•$3H_2O$ (54 mmol), and CB (0.4 g) were dissolved/dispersed in a mixture solution containing $HOCH_2CH_2OH$ (120.0 mL) and deionized water (120.0 mL) to form a homogeneous slurry, which was subsequently sealed in a stainless steel autoclave and heated at 200 ℃ for 48 h to obtain the desired product. The resulting precipitate was collected by centrifugation; washed with distilled water and absolute ethanol; and finally, dried in vacuum at 80 ℃ for 24 h to obtain the $ZnFe_2O_4$/CB composite. Other catalysts were synthesized the same as the $ZnFe_2O_4$/CB, except use α-$Al_2O_3$, γ-$Al_2O_3$, GCB, CNT to replace CB.

### Catalytic activity of supported catalyst

Fig. S6 show XRD patterns of supported $ZnFe_2O_4$ catalysts. the observed diffraction peaks from the XRD patterns at 2θ values of 30.1, 35.6, 43.4, 57.3, and 62.8$^o$ correspond to the lattice planes of (220), (311), (400), (511), and (440) respectively, indicating the formation of $ZnFe_2O_4$ (JCPDS 01-089-1012), While the others peaks correspond to lattice planes of supports, respectively. The crystal size of corresponding bare $ZnFe_2O_4$ and supported $ZnFe_2O_4$ catalysts was calculated by Scherrer equation and summarized in Table S8. When $ZnFe_2O_4$ supported on α-$Al_2O_3$, γ-$Al_2O_3$, CB, GCB and CNT, size of $ZnFe_2O_4$ nanoparticles become smaller. As we can see from Figure S7a, the component of gas product of supported catalysts was almost the same with bare $ZnFe_2O_4$ catalyst,

except that $ZnFe_2O_4/\gamma\text{-}Al_2O_3$ had more $H_2$ and less $CH_4$. Fig. S7b presents the liquid products of methanol conversion over $ZnFe_2O_4$ supported catalysts. After $ZnFe_2O_4$ loaded on different supports, reaction activity of conversion methanol to hydrocarbons decreased. This may be that the addition of supports covers the active sites of $ZnFe_2O_4$.

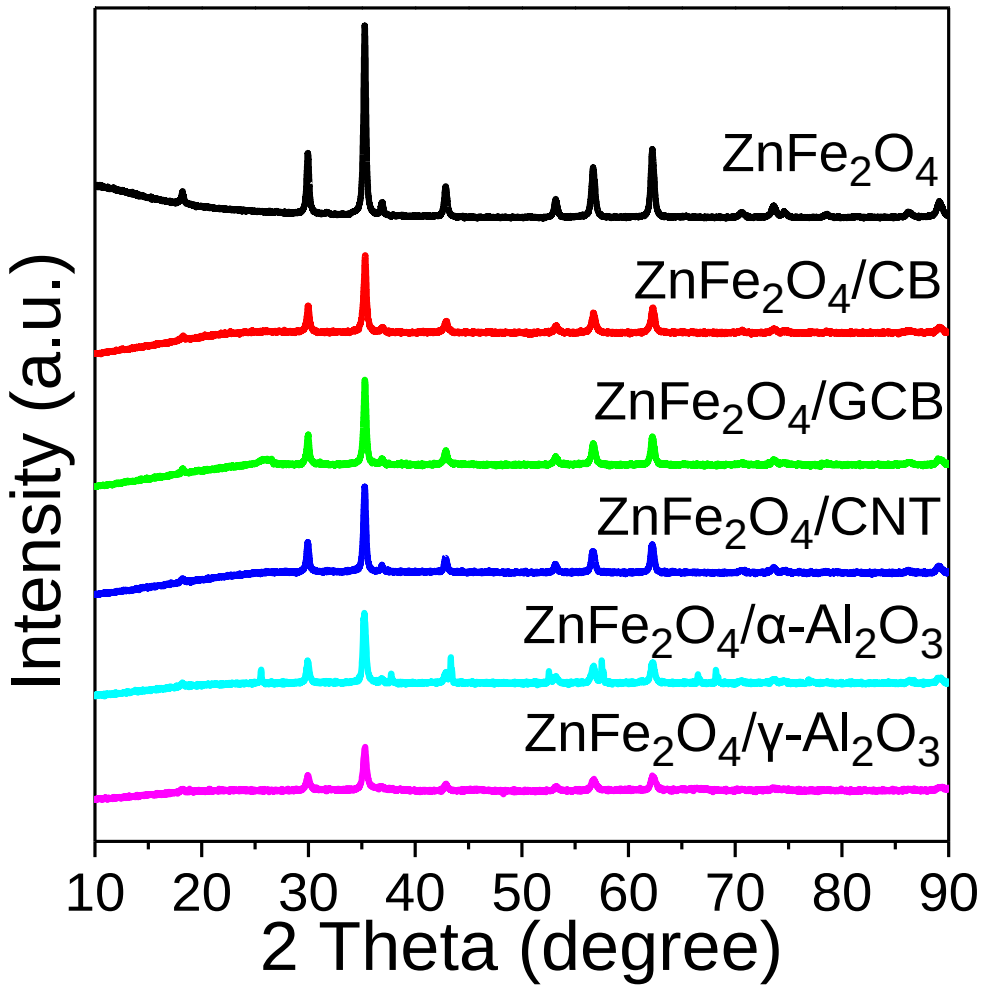


**Fig. S6** XRD patterns of supported $ZnFe_2O_4$ catalysts.

**Table S8** Crystal size of bare and supported $ZnFe_2O_4$ catalysts.

| Sample | Crystal size [a] |
|---|---|
| $ZnFe_2O_4$ | 29.4 |
| $ZnFe_2O_4/\alpha\text{-}Al_2O_3$ | 22.8 |
| $ZnFe_2O_4/\gamma\text{-}Al_2O_3$ | 22.6 |
| $ZnFe_2O_4$/CB | 26.6 |
| $ZnFe_2O_4$/GCB | 27.0 |
| $ZnFe_2O_4$/CNT | 27.9 |

[a] Crystal size, derived from XRD by Debye−Scherrer equation.

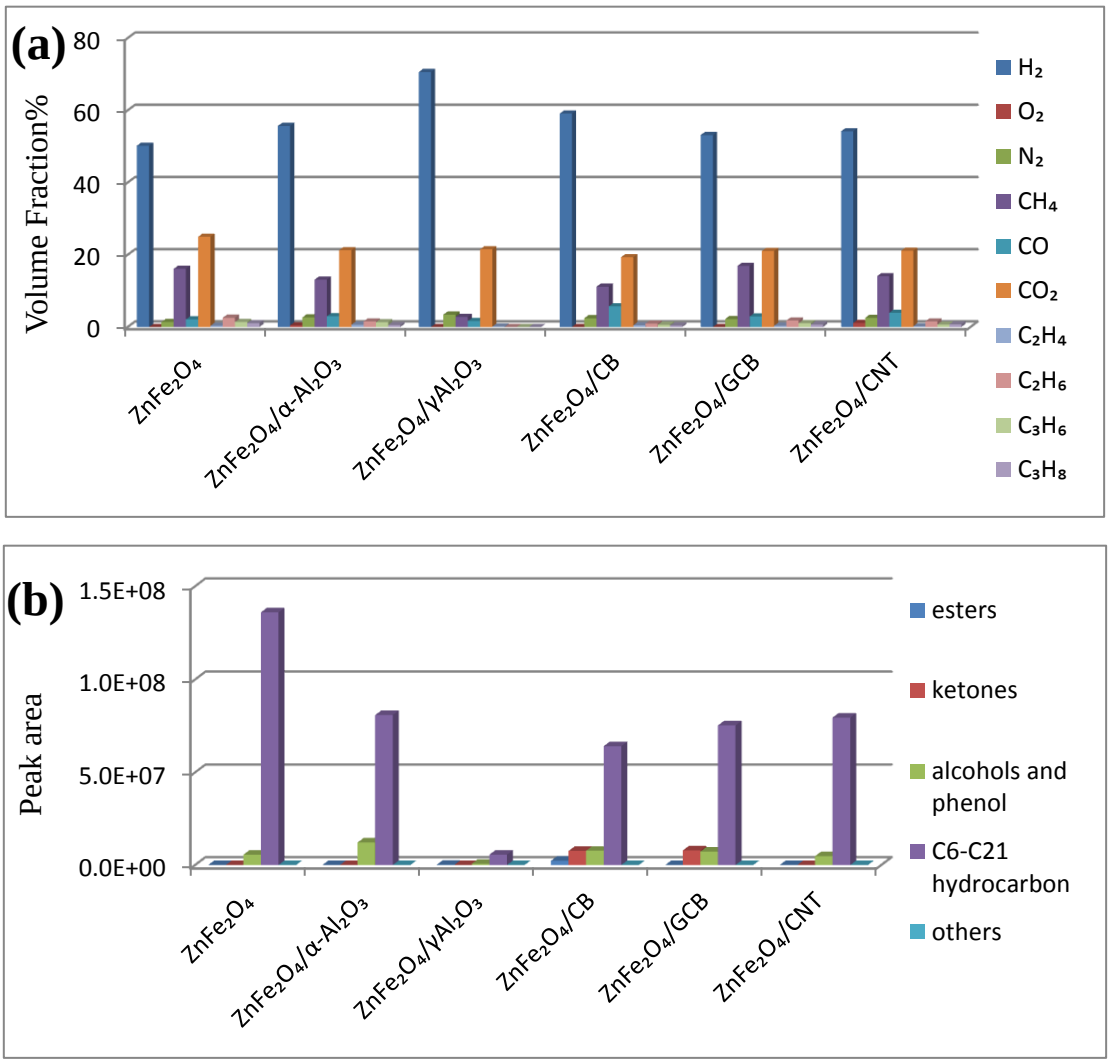


**Fig. S7** Distributions of gas (a) and liquid (b) products over supported catalysts. (Reaction conditions: 0.5 g catalyst, 30 mL methanol, 120 min, 300 $^{o}$C.)