# Supporting Information

## Effects of Cu species on liquid-phase partial oxidation of methane with $H_2O_2$ over Cu-Fe/ZSM-5 catalysts

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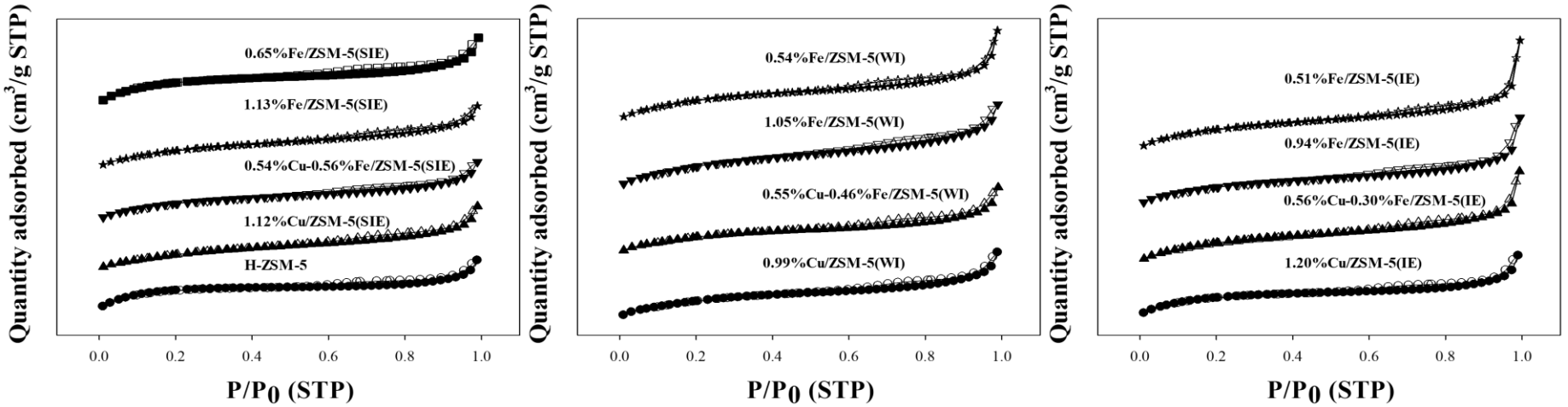



**Figure S1.** $N_2$ adsorption and desorption isotherm of the prepared catalyst.

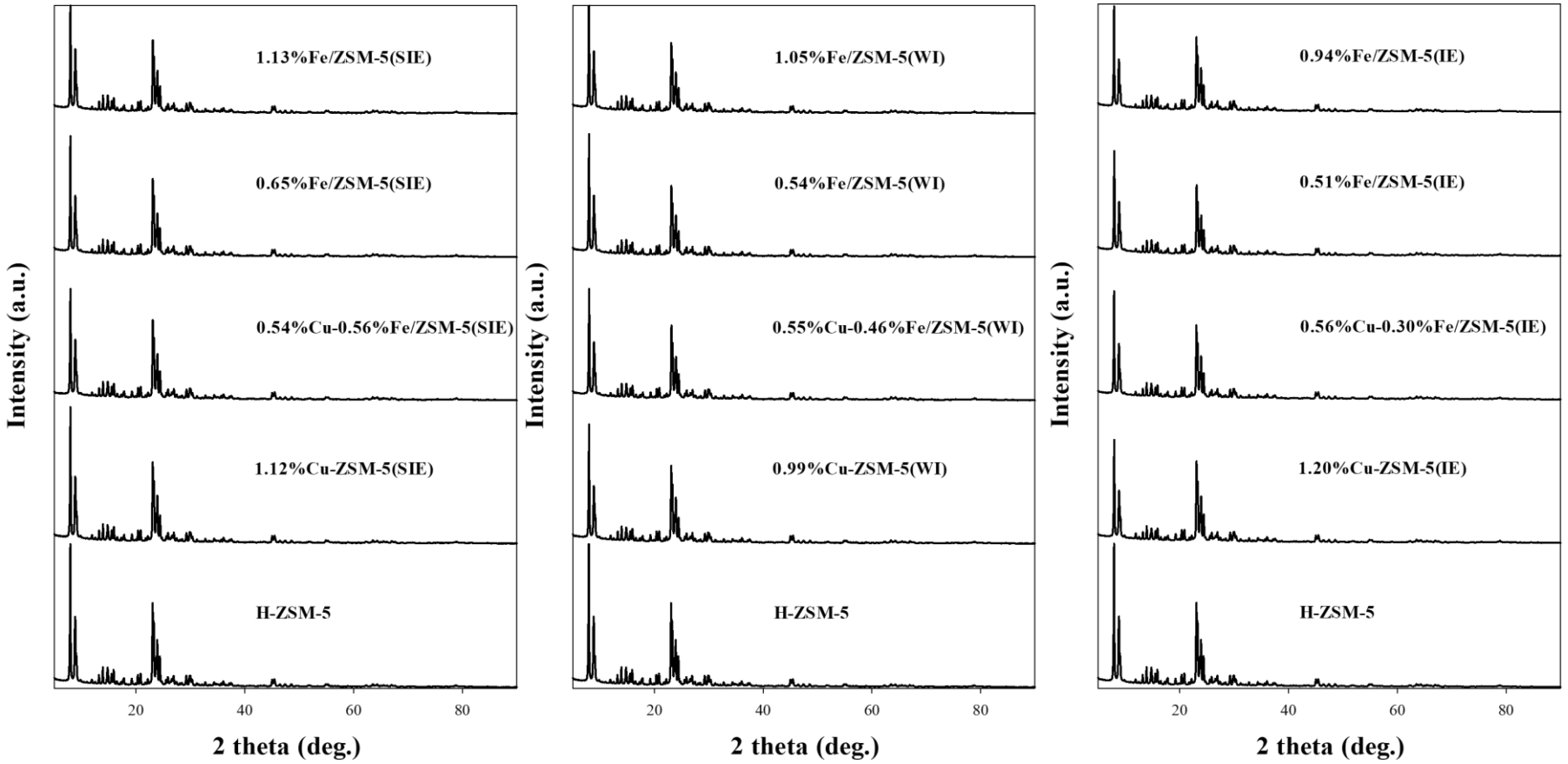
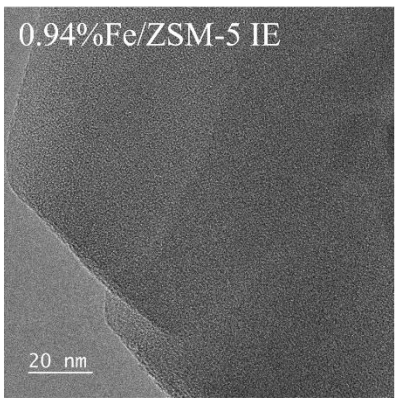
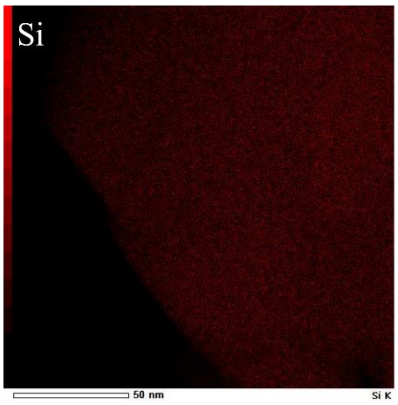
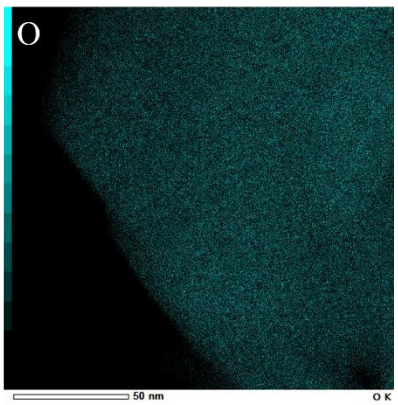
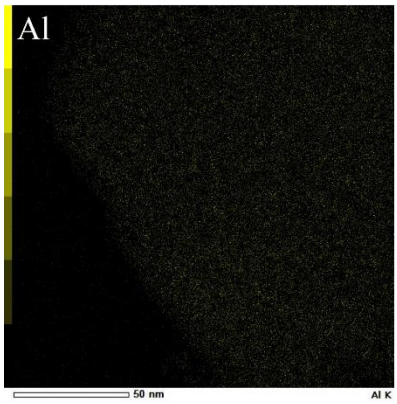


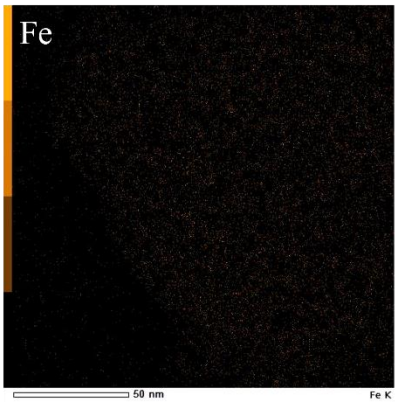

**Figure S2.** XRD patterns of the prepared catalysts.

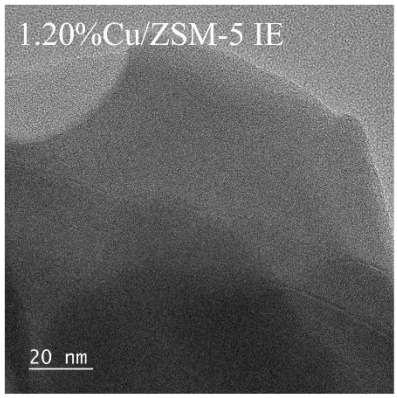

0.94%Fe/ZSM-5 IE
20 nm

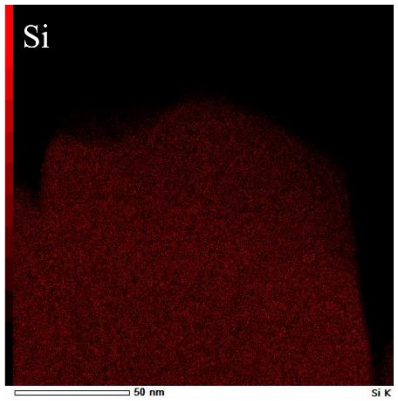

Si
50 nm
Si K

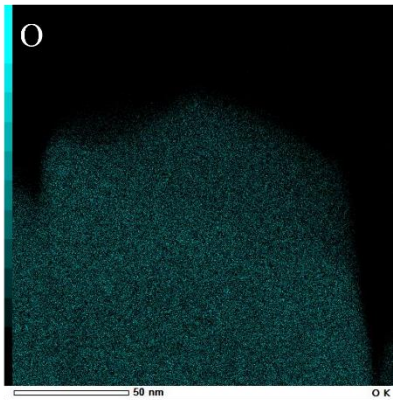

O
50 nm
O K

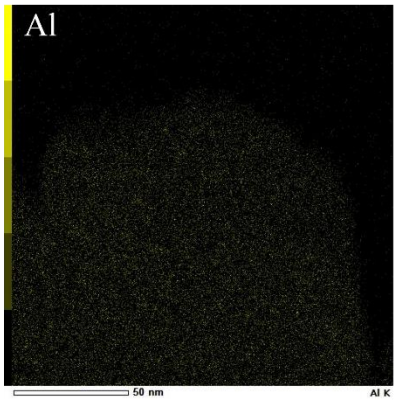

Al
50 nm
Al K

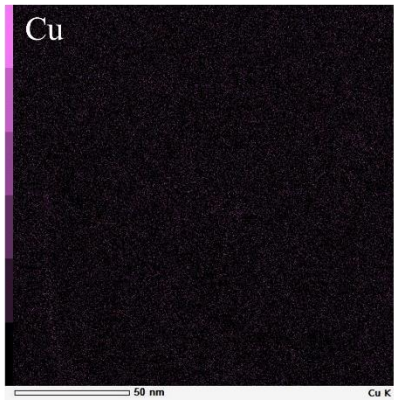

Fe
50 nm
Fe K

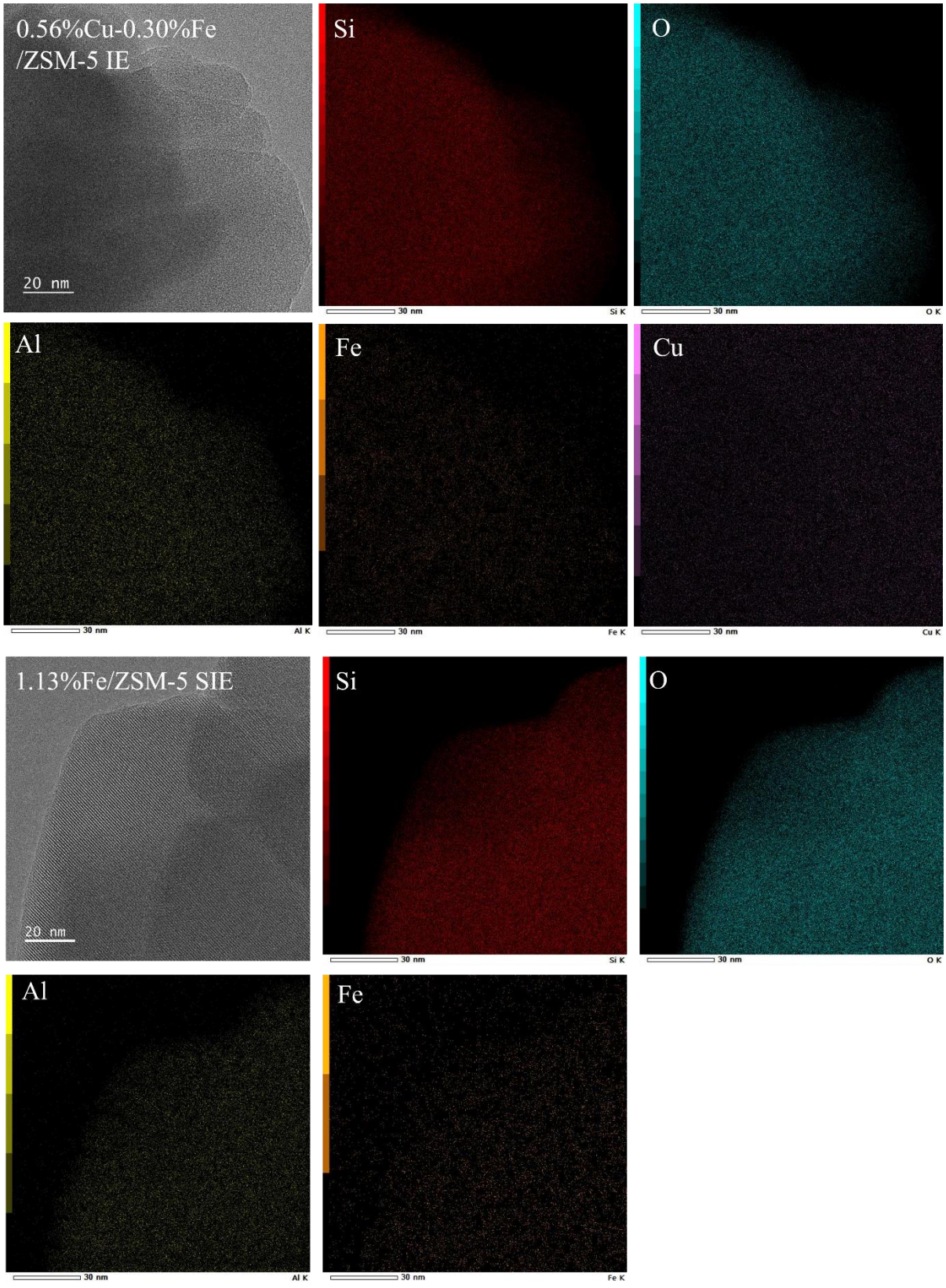

1.20%Cu/ZSM-5 IE
20 nm


Si
50 nm
Si K


O
50 nm
O K


Al
50 nm
Al K


Cu
50 nm
Cu K


0.56%Cu-0.30%Fe
/ZSM-5 IE
20 nm
Si
30 nm
Si K
O
30 nm
O K
Al
30 nm
Al K
Fe
30 nm
Fe K
Cu
30 nm
Cu K
1.13%Fe/ZSM-5 SIE
20 nm
Si
30 nm
Si K
O
30 nm
O K
Al
30 nm
Al K
Fe
30 nm
Fe K

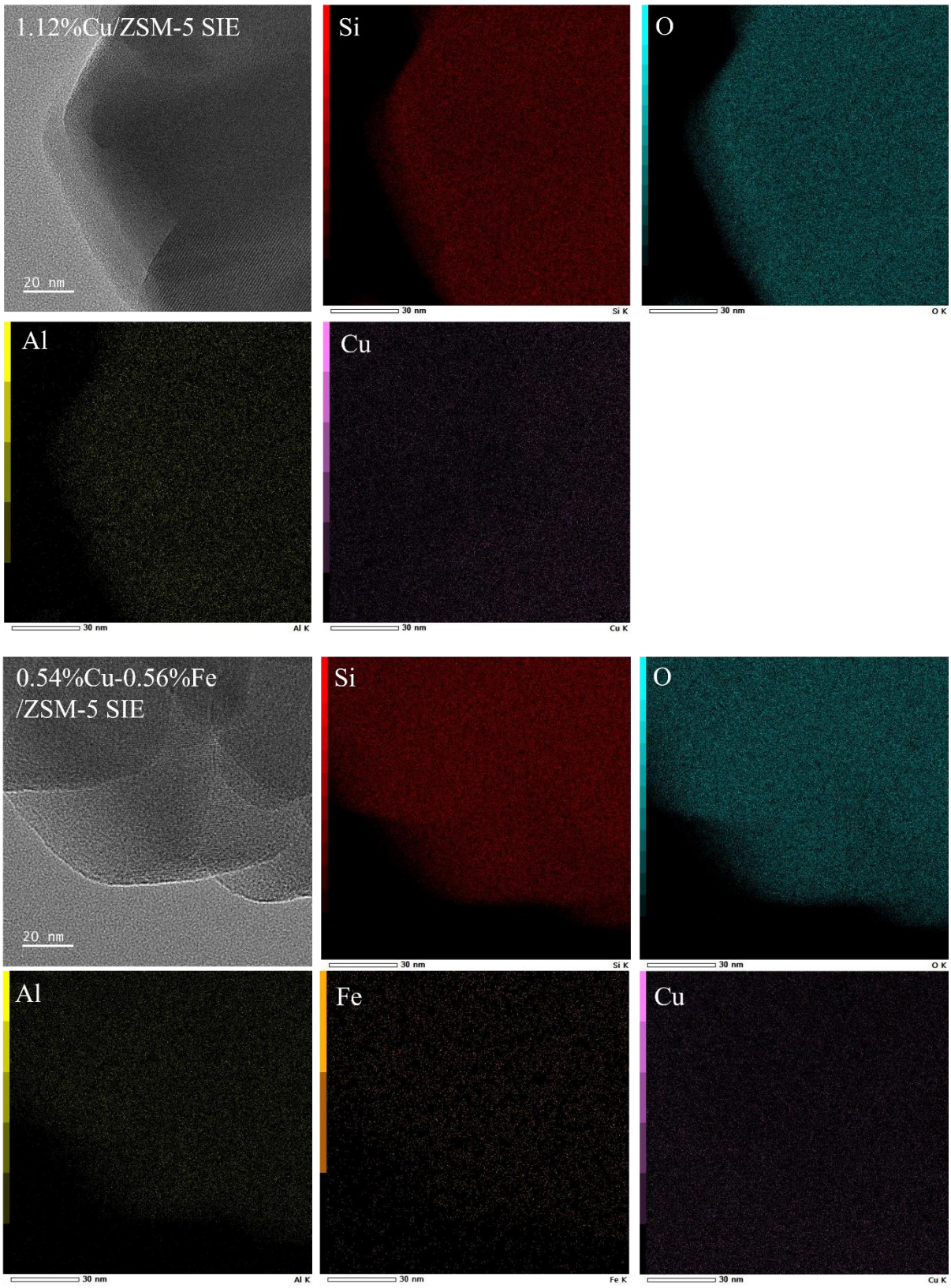



**Figure S3.** TEM images and EDS mapping results for the prepared catalysts.

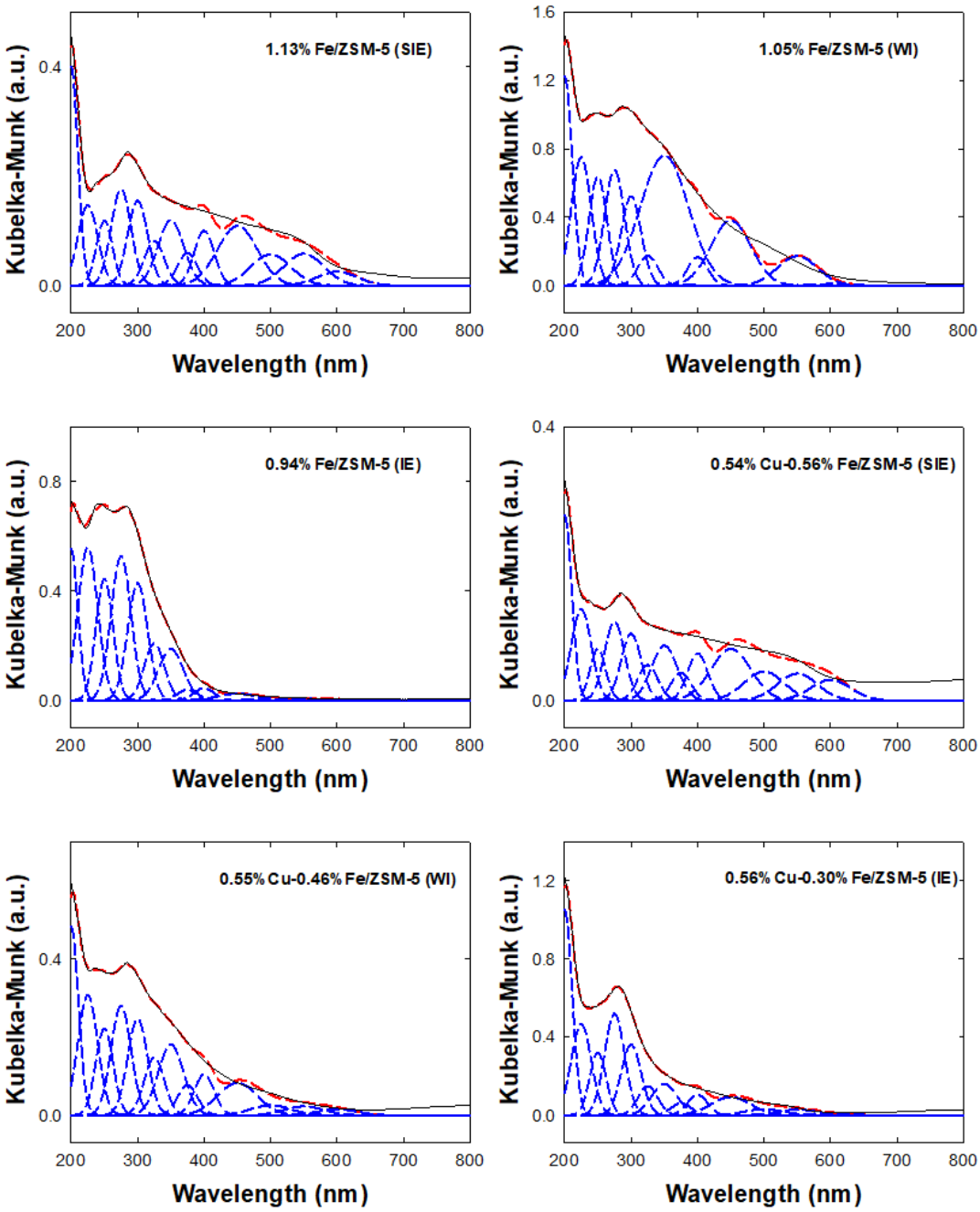
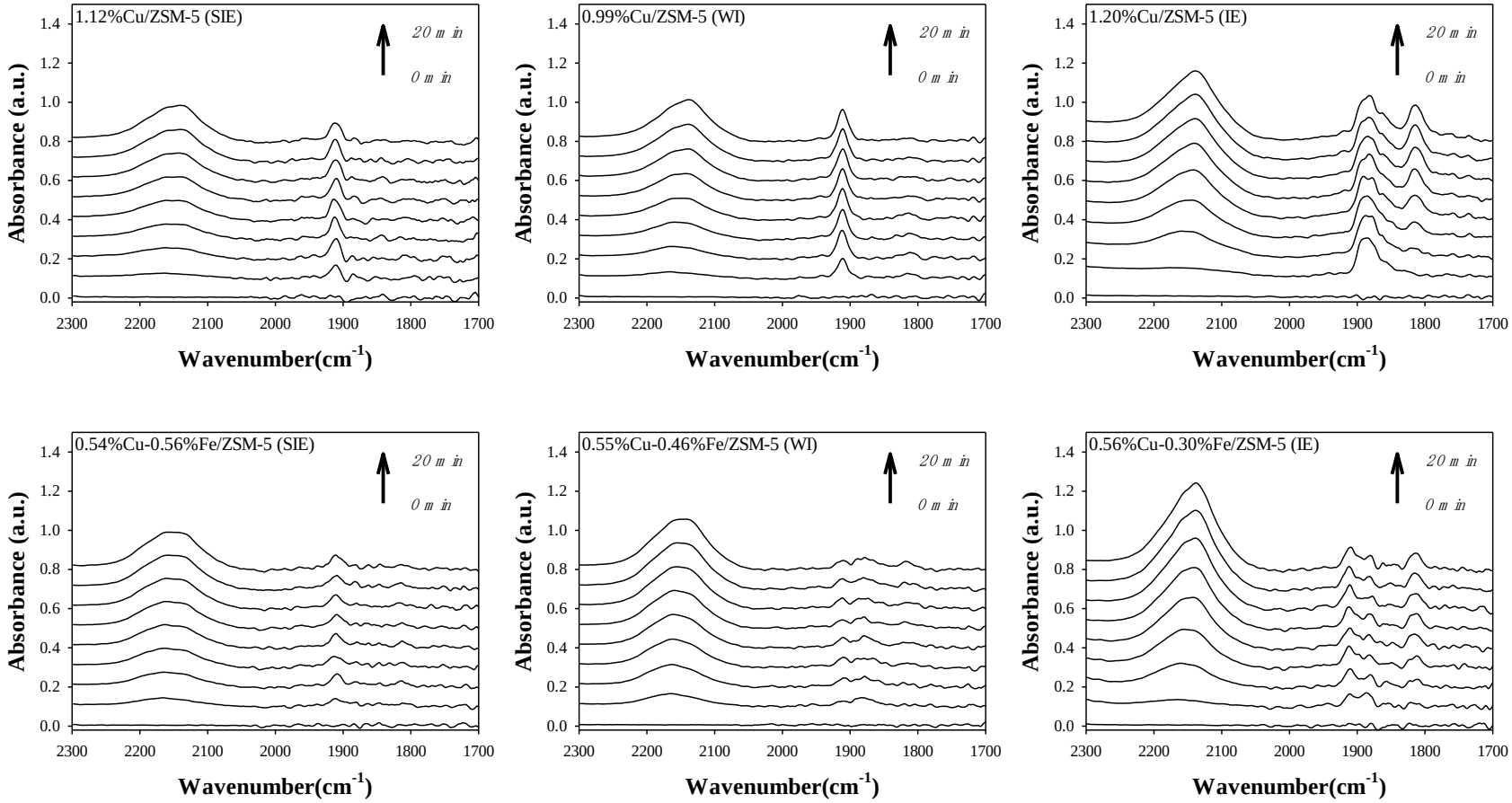



**Figure S4.** Deconvolution of UV-Vis spectra for the catalysts prepared with different methods.


1.12%Cu/ZSM-5 (SIE)
0.99%Cu/ZSM-5 (WI)
1.20%Cu/ZSM-5 (IE)
0.54%Cu-0.56%Fe/ZSM-5 (SIE)
0.55%Cu-0.46%Fe/ZSM-5 (WI)
0.56%Cu-0.30%Fe/ZSM-5 (IE)
20 min
0 min
Absorbance (a.u.)
Wavenumber(cm-1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
2300
2200
2100
2000
1900
1800
1700

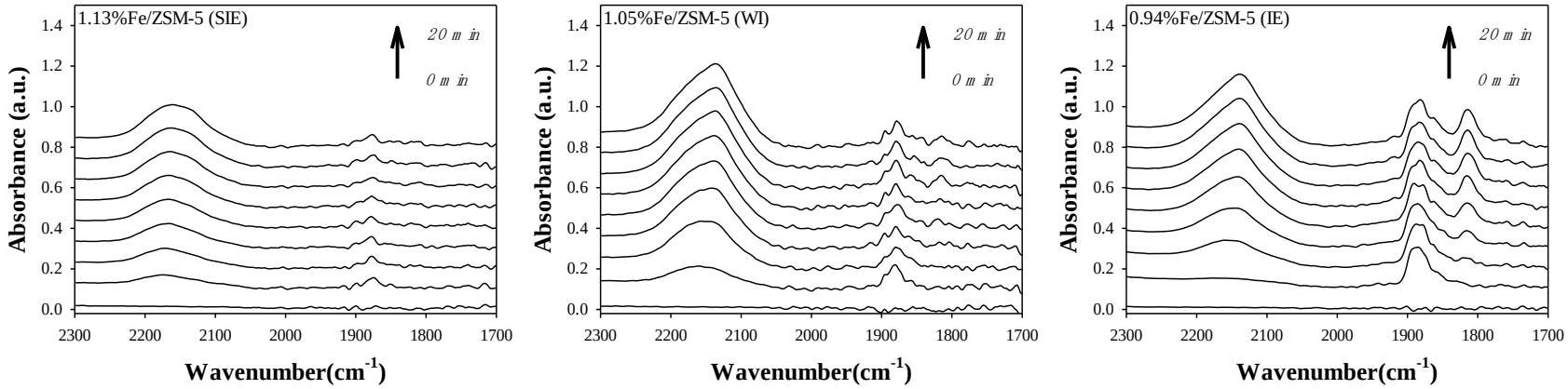



**Figure S5.** NO-FTIR spectra for the catalysts prepared with different methods from 0 to 20 min.

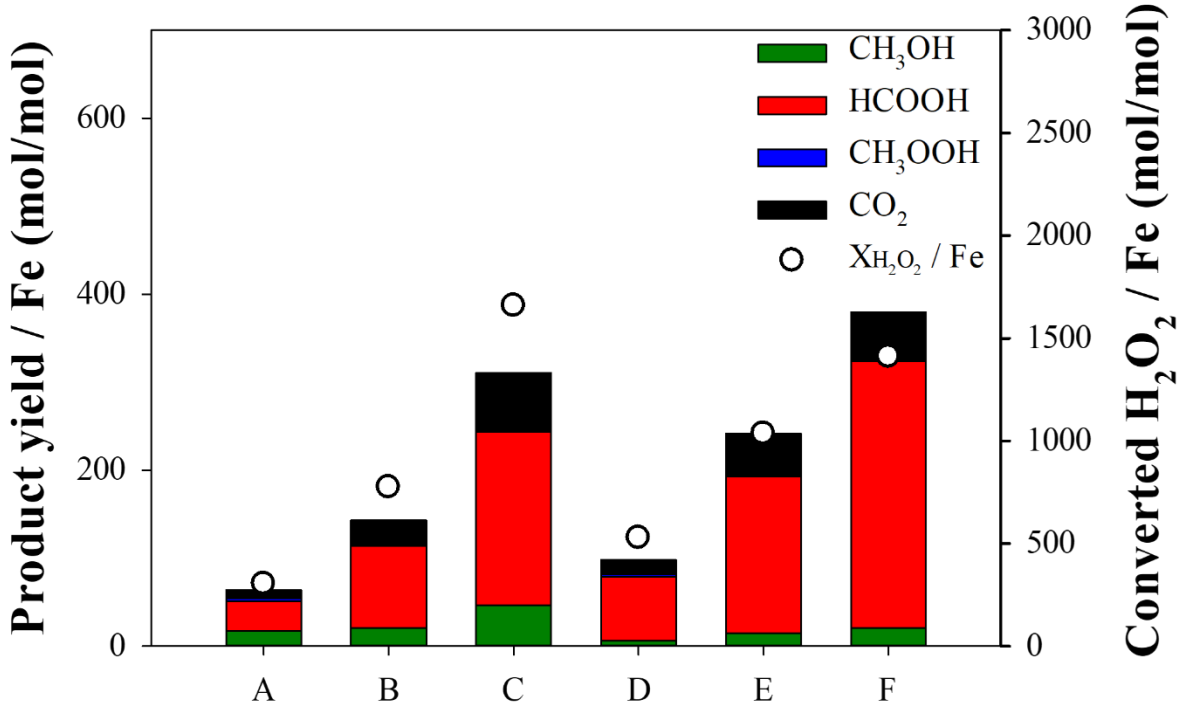



**Figure S6.** Partial oxidation of methane over 0.54%Cu-0.56%Fe/ZSM-5(SIE) (A), 0.55%Cu-0.46%Fe/ZSM-5(WI) (B), 0.56%Cu-0.30%Fe/ZSM-5(IE) (C), 0.65%Fe/ZSM-5(SIE) (D), 0.54%Fe/ZSM-5(WI) (E), and 0.51%Fe/ZSM-5(IE) (F). Reaction conditions: 50 mg catalyst, 31 bar methane, 0.277 M $H_2O_2$, liquid volume = 30 mL, reaction temperature = 50 ℃.

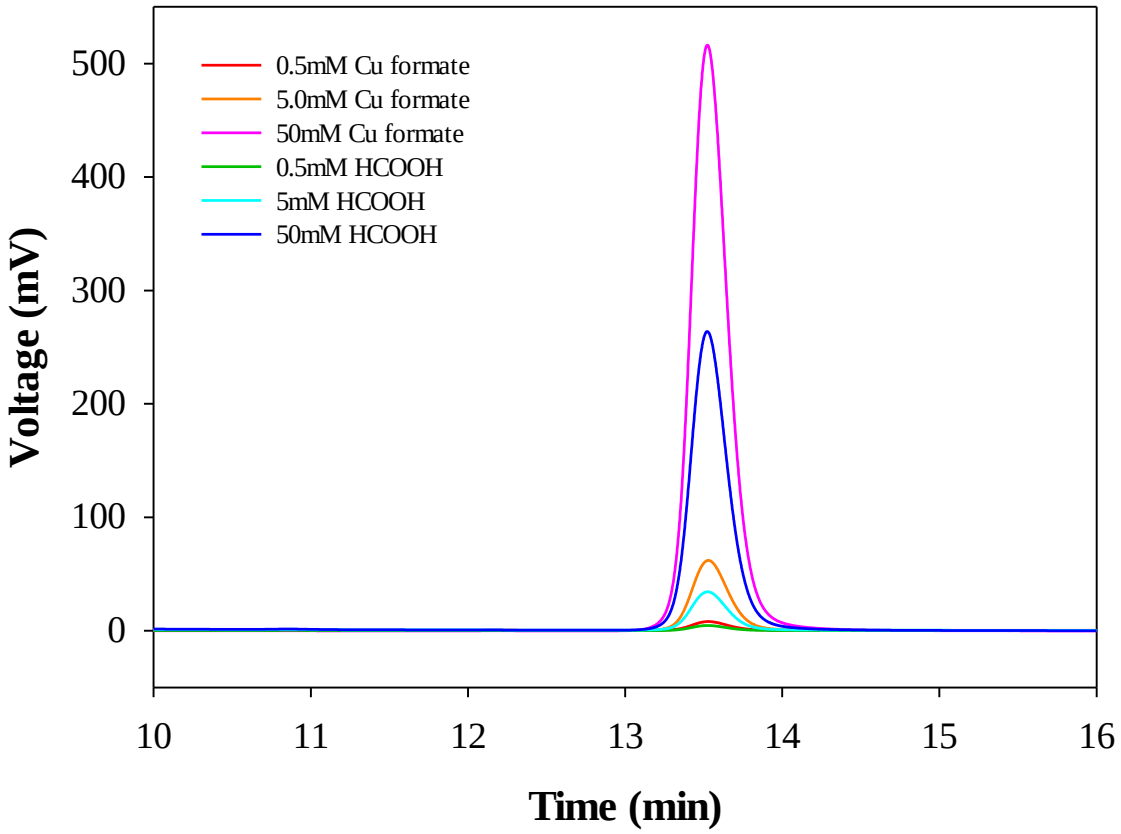



**Figure S7.** HPLC chromatograms for the standard solutions of different HCOOH and $Cu(HCOO)_2$ concentrations.

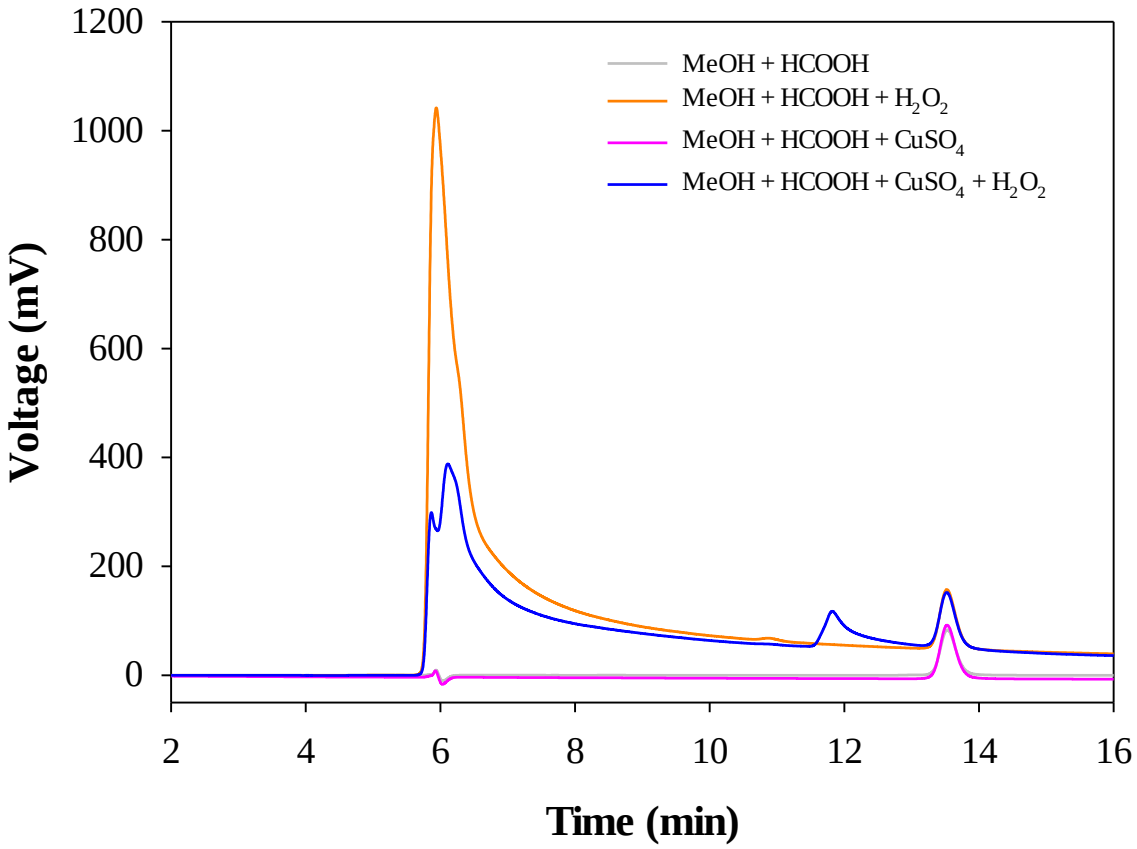



**Figure S8.** HPLC chromatograms for the standard solutions with different compositions.

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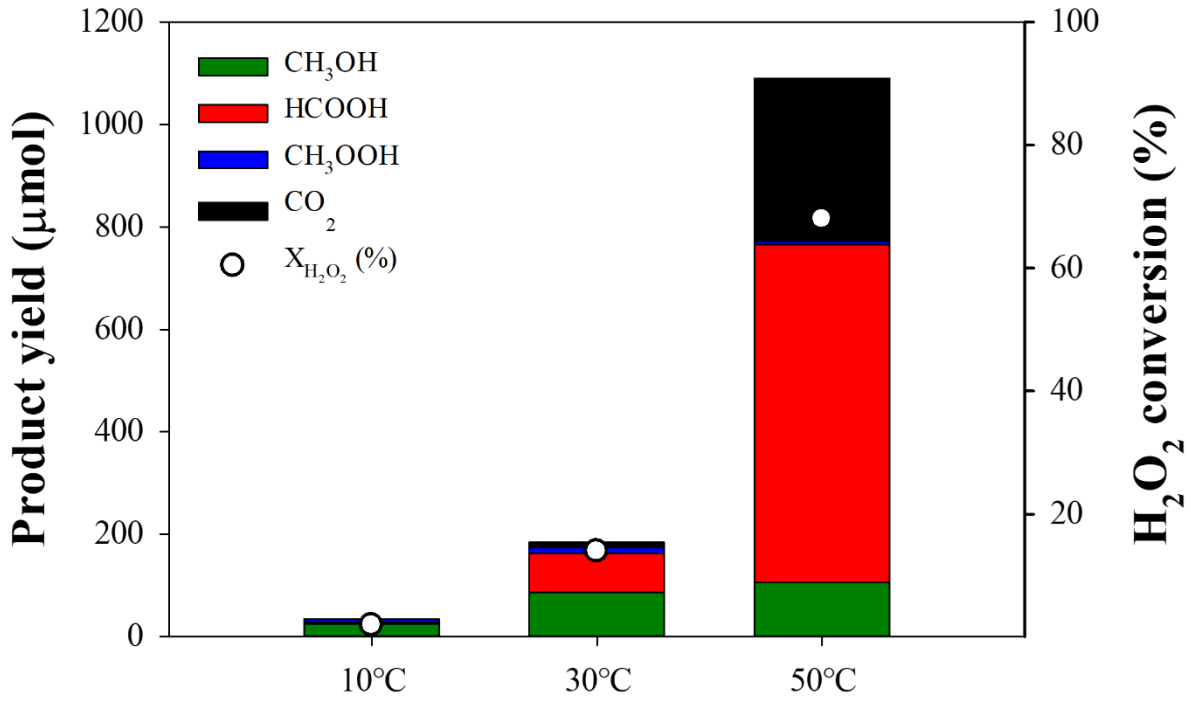



**Figure S9**. Partial oxidation of methane over Cu-Fe/ZSM-5(IE) catalyst at different temperatures. Reaction conditions: 50 mg catalyst, 31 bar methane, 0.277 M $H_2O_2$, liquid volume = 30 mL.

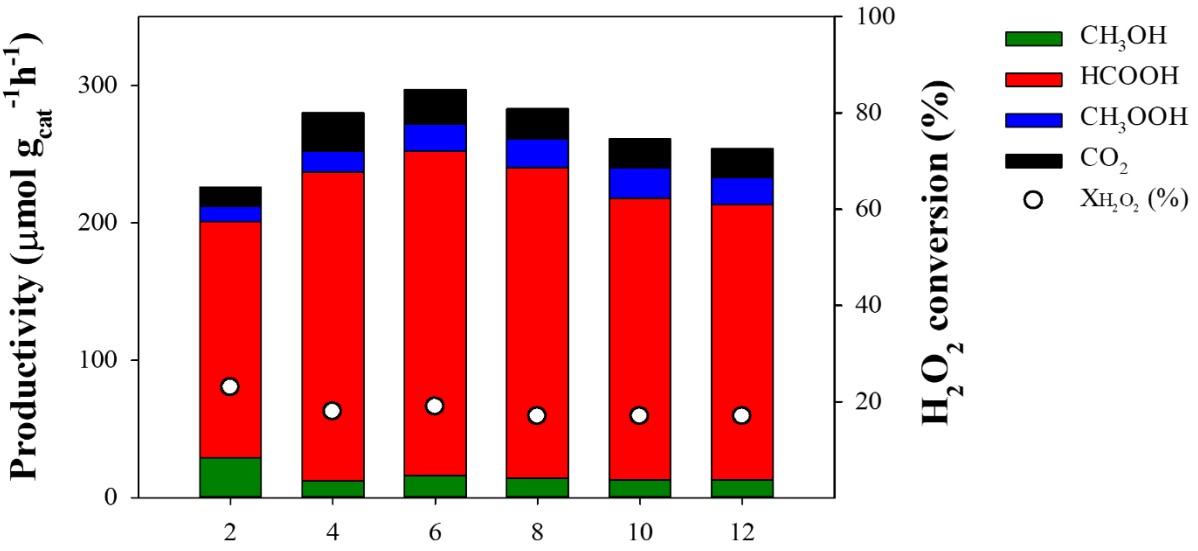



**Figure S10.** Continuous aqueous phase oxidation of methane with $H_2O_2$ in a flow reactor over H-ZSM-5. Reaction conditions: $P_{CH4}$ = 21 bar, $F_{CH4}$= 50 mL/min, [$H_2O_2$]= 0.123 mol/L, $F_{H2O2}$= 0.25 mL/min, $W_{cat.}$ = 0.2g, Temperature = 50 ℃.

**Table S1.** The fraction of each Fe species estimated from the UV-vis band in Fig. S4 for Fe/ZSM-5 and Cu-Fe/ZSM-5 catalysts.

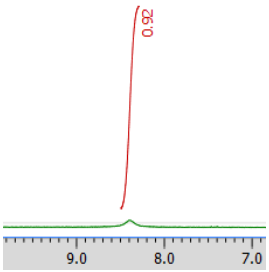
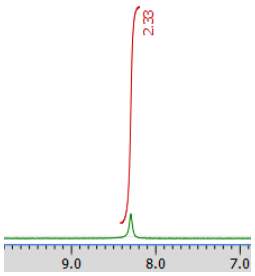
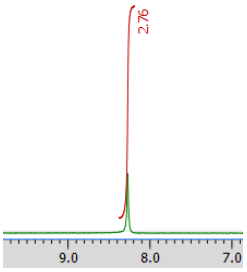
| Catalyst | Fraction of UV-Vis band (%) | | | |
|---|---|---|---|---|
| | **200~250 nm** | **250~350 nm** | **350~450 nm** | **>450 nm** |
| 0.54%Cu-0.56%Fe/ZSM-5(SIE) | 20 | 28 | 20 | 32 |
| 1.13%Fe/ZSM-5(SIE) | 20 | 32 | 22 | 27 |
| 0.55%Cu-0.46%Fe/ZSM-5(WI) | 27 | 42 | 18 | 13 |
| 1.05%Fe/ZSM-5(WI) | 23 | 40 | 23 | 14 |
| 0.56%Cu-0.30%Fe/ZSM-5(IE) | 33 | 43 | 13 | 11 |
| 0.94%Fe/ZSM-5(IE) | 34 | 55 | 9 | 3 |

**Table S2.** Catalytic activity result of partial oxidation of methane in this study at 50 °C.[a]

| Entry | Catalyst | Cu (mM) | $X_{H2O2}$ (%) | Product (mmol) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $CH_3OH$ | HCOOH | $CH_3OOH$ | $CO_2$ | Total |
| 1 | CuO | 3.93 | 99 | 0.000 | 0.013 | 0.000 | 0.000 | 0.013 |
| 2 | $Cu_2O$ | 3.93 | 89 | 0.002 | 0.024 | 0.012 | 0.019 | 0.057 |
| 3 | $Cu(CH_3COO)_2$ | 4.41 | 99 | 0.004 | 0.040 | 0.000 | 0.030 | 0.074 |
| 4 | $Cu(NO_3)_2$ | 4.41 | 29 | 0.004 | 0.059 | 0.038 | 0.023 | 0.124 |
| 5 | $CuSO_4$ | 4.41 | 30 | 0.009 | 0.084 | 0.028 | 0.028 | 0.149 |
| 6 | $CuSO_4$ | 0.147 | 15 | 0.017 | 0.010 | 0.017 | 0.000 | 0.044 |

[a]Recation condition: 30 mL of 0.277 M $H_2O_2$, 95 mL of $CH_4$ at 31 bar, 50 mg of catalyst, reaction time = 1 h.

**Table S3.** The Cu concentration in the product solution, $^{1}$H-NMR spectra, and concentrations of HCOOH determined with $^{1}$H-NMR and HPLC during the cyclic test.[a]

| The number of experiment for the cyclic test | 1 | 2 | 3 |
|---|---|---|---|
| Cu concentration[b] (ppm) | 5.20 | 1.89 | 0.8 |
| $^{1}$H-NMR spectra |  |  |  |
| HCOOH concentration[c] (mM) | 7.6 | 14.9 | 17.1 |
| HCOOH concentration[d] (mM) | 22 | 16.5 | 18 |



[a]0.56%Cu-0.30%Fe/ZSM-5(IE) catalyst was used and the other reaction conditions are same with those in Fig. 5.

[b]Cu concentration was determined with ICP – OES.

[c]HCOOH concentration was determined with $^{1}$H-NMR.

[d]HCOOH concentration was determined with HPLC.

**Table S4.** Concentrations of HCOOH in different stand solutions determined with $^1$H-NMR and HPLC.

| Entry | Standard solution | Concentration of HCOOH determined with $^1$H-NMR (M) | Concentration of HCOOH determined with HPLC (M) |
|---|---|---|---|
| 1 | 0.02 M HCOOH + 0.0015 M MeOH | 0.02 | 0.02 |
| 2 | 0.02 M HCOOH + 0.0015 M MeOH + 0.277 M $H_2O_2$ | 0.02 | 0.02 |
| 3 | 0.02 M HCOOH + 0.0015 M MeOH + 0.26 mM $CuSO_4$ | 0.003 | 0.02 |
| 4 | 0.02 M HCOOH + 0.0015 M MeOH + 0.26 mM $CuSO_4$ + 0.277 M $H_2O_2$ | 0.003 | 0.02 |

**Table S5.** The amount of Cu leached from Cu/ZSM-5 with different concentrations of HCOOH.

| Entry | Condition | The percentage of Cu leached (%) |
|---|---|---|
| 1 | HCOOH 0.5 mmol + 1.20% Cu/ZSM-5 (IE) | 40 |
| 2 | HCOOH 1 mmol + 1.20% Cu/ZSM-5 (IE) | 49 |
| 3 | HCOOH 2 mmol + 1.20% Cu/ZSM-5 (IE) | 55 |

Reaction conditions: 30 mL of 0.277 M $H_2O_2$, 95 mL of $N_2$ at 31 bar, 50 mg of catalyst, reaction temperature = 50 ℃, reaction time = 1 h.

**Table S6.** The activity comparison among catalysts reported previously and in this work during continuous liquid-phase selective oxidation of methane in a flow reactor.

| Entry | Catalyst | $H_2O_2$ Conversion (%) | Selectivity (%) | | | | Total Productivity (mol $kg_{cat}^{-1}h^{-1}$) | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | $CH_3OH$ | HCOOH | $CH_3OOH$ | $CO_2$ | | |
| 1 | H–ZSM-5[a] | 64.1 | 8.7 | 81.6 | 1.6 | 8.1 | 0.081 | [65] |
| 2 | 1.5%Cu/ZSM-5[a] | 52.8 | 89.1 | 0.0 | 1.0 | 9.9 | 0.065 | [65] |
| 3 | 1.5%Fe/ZSM-5[a] | 93.3 | 15.1 | 71.4 | 0.0 | 13.6 | 0.032 | [65] |
| 4 | 0.4%Fe-0.4%Cu/ZSM-5[a] | 82.9 | 39.2 | 56.2 | 0.8 | 3.8 | 0.049 | [65] |
| 5 | 1.5%Fe-1.5%Cu/ZSM-5[a] | 92.9 | 92.2 | 0.0 | 0.0 | 7.8 | 0.081 | [65] |
| 6 | H–ZSM-5[b] | 19 | 7 | 78 | 7 | 8 | 0.267 | This study |
| 7 | 0.51%Fe/ZSM-5(IE)[b] | 90 | 5 | 78 | 1 | 16 | 1.125 | This study |
| 8 | 0.56%Cu-0.30%Fe/ZSM-5(IE)[b] | 65 | 17 | 66 | 1 | 16 | 0.933 | This study |

[a]Reaction conditions: $P_{CH4}$ = 21 bar, $F_{CH4}$= 10 mL/min, [$H_2O_2$] = 0.123 mol/L, $F_{H2O2}$= 0.25 mL/min, $W_{cat.}$ = 1.5g, Temperature = 50 ℃.

[b]Reaction conditions: $P_{CH4}$ = 21 bar, $F_{CH4}$ = 50 mL/min, [$H_2O_2$] = 0.123 mol/L, $F_{H2O2}$ = 0.25 mL/min, $W_{cat.}$ = 0.2g, Temperature = 50 ℃.

**Table S7.** The concentration of Cu species in the product solution during continuous liquid-phase selective oxidation of methane over 0.56%Cu-0.30%Fe/ZSM-5(IE) in a flow reactor.

| Time on stream (h) | Liquid volume collected (mL) | Concentration of Cu in the solution (ppm) | The percentage of Cu leached in the total amount of Cu in the fresh catalyst (%) |
|---|---|---|---|
| 2 | 27 | 5.44 | 15 |
| 4 | 26.5 | 3.84 | 10 |
| 6 | 29 | 2.94 | 8 |
| 8 | 27 | 1.75 | 5 |
| 10 | 27 | 1.25 | 3 |
| 12 | 27 | 1.73 | 5 |
| 14 | 25 | 1.71 | 5 |

Reaction conditions: $P_{CH4}$ = 21 bar, $F_{CH4}$ = 50 mL/min, [$H_2O_2$] = 0.123 mol/L, $F_{H2O2}$ = 0.25 mL/min, $W_{cat.}$ = 0.2g, Temperature = 50 ℃.