Electronic Supplementary Information

Maximizing Methanol Selectivity over Microporous FeS-1 Catalyst via Aqueous-phase Partial Oxidation of Methane with H_2O_2

Balashanmugham Venugopal[1], Niket S. Kaisare[1] and Parasuraman Selvam[2,3*]

[1]*National Center for Catalysis Research and Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600 036, India*

[2]*National Center for Catalysis Research and Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

[3]*Research Organization for Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan*

*Corresponding Author: selvam@faculty.iitm.ac.in

The supplementary information (PDF) file contains Tables and Figures.

Table S1. The acid properties of various FeS-1 (FC) deduced from NH_3-TPD measurements.

Catalyst	[a]T_{max} (°C)		Acid content (mmol g^{-1})		
	LT	HT	180-230°C	290-320°C	Total acid sites
FeS-1 (276)	206	298	0.062	0.0231	0.0851
FeS-1 (200)	194	316	0.080	0.0313	0.1111
FeS-1 (134)	220	316	0.107	0.0743	0.1813

[a]The desorption peak maximum temperature; LT and HT represent the low-temperature and high-temperature regions of the TPD traces, respectively.

Table S2. The relative signal intensities of various iron species deduced from EPR spectral data.

Catalyst	Type	$g_1 = 4.3$ (Fe_{FW})	$g_2 = 2.0$ (Fe_{EFW})
FeS-1 (276)	Fresh	4204	27492
	Deferrated	4104	16057
FeS-1 (200)	Fresh	4844	56423
	Deferrated	4294	23348
FeS-1 (134)	Fresh	5509	115320
	Deferrated	4857	54121

Table S3. Deconvoluted DRUV-VIS spectral data of various MFI-based materials.

Sample	Fe content (wt %)	λ_1 (220 *nm*)	λ_2 (246 *nm*)	λ_3 (280-310 *nm*)
Fresh Catalyst				
FeS-1(276)	0.47	0.10	0.23	0.12
FeS-1(200)	0.62	0.12	0.31	0.15
FeS-1(134)	0.75	0.15	0.36	0.18
FeZSM-5 (138)	0.69	0.06	0.16	0.38
Deferrated Catalyst				
FeS-1(276)	0.37	0.10	0.20	0.08
FeS-1(200)	0.47	0.11	0.26	0.09
FeS-1(134)	0.58	0.13	0.33	0.11
FeZSM-5 (138)	0.47	0.07	0.22	0.19

Table S4. Methane partial oxidation data of various Fe-exchanged ZSM-5.

Catalyst	Nominal Fe content (wt. %)	H_2O_2 (%)	Y_{MeOH} (μmol)	Y_{HCOOH} (μmol)
Fe–ZSM-5 (FC)	0.50	19	15	35
Fe–ZSM-5 (FC)	1.00	45	28	62
Fe–ZSM-5 (FC)	1.50	58	47	100
Fe–ZSM-5 (DC)	0.33	15	12	11
Fe–ZSM-5 (DC)	0.56	38	23	33
Fe–ZSM-5 (DC)	0.90	46	41	48

Reaction Conditions: Catalyst amount = 25 mg; [H_2O_2] = 0.5 M; T = 50 °C; t = 30 min; Stirring speed = 570 rpm.

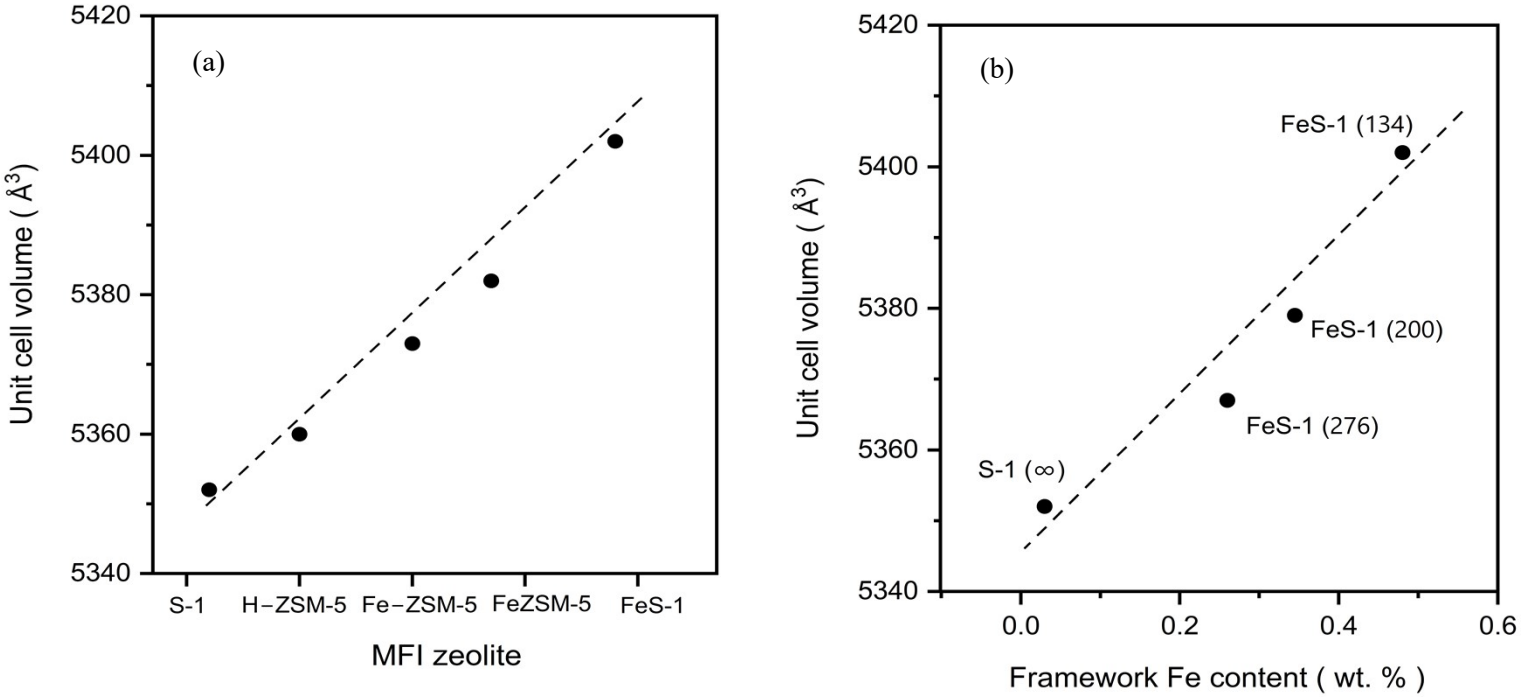

Figure S1. (a) The unit cell volume variation, as per the data projected in Table 1, for various MFI-based zeolites. (b) The unit cell volume variation, as per the data projected in Table 1, for various iron silicalites.

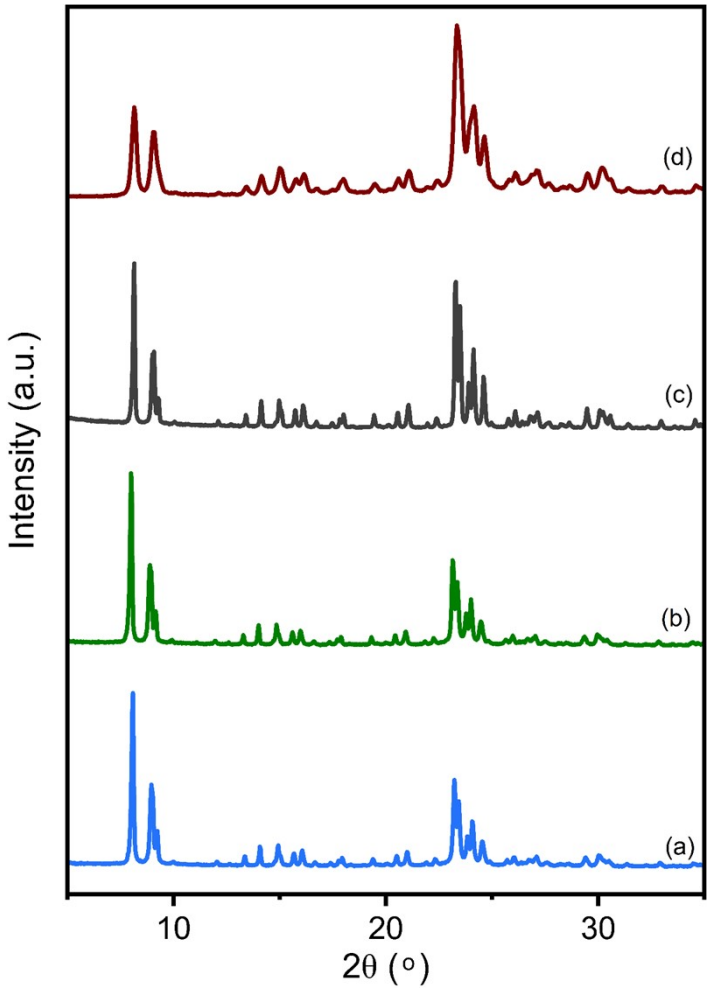

Figure S2. Powder XRD patterns of Fe/MFI (FC): (a) ZSM-5 (30) (b) Fe–ZSM-5(30) (c) FeZSM-5 (d) FeS-1 (100).

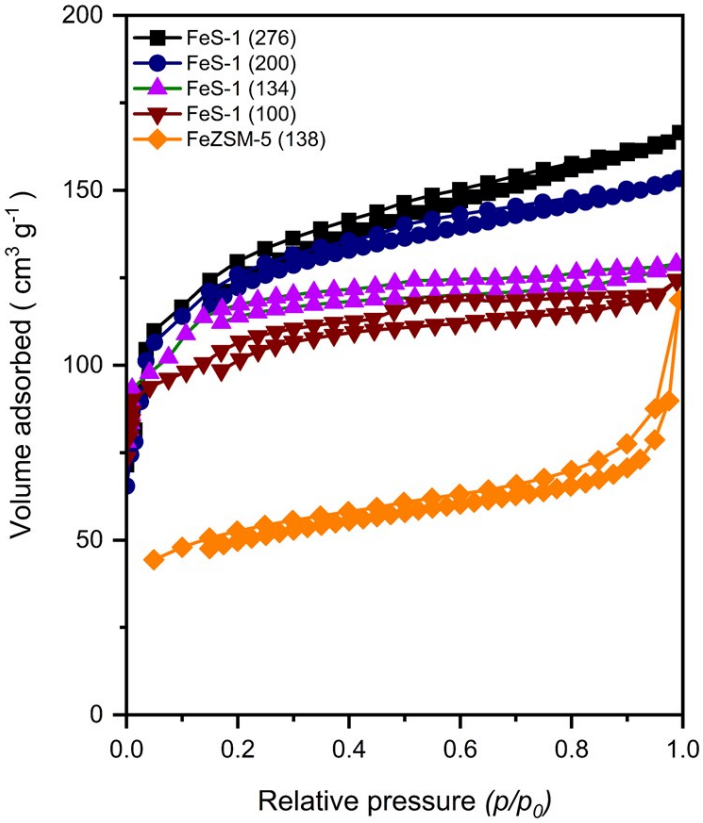

Figure S3. N_2 isotherms for calcined FeS-1 catalysts at 77 K after activating the catalysts.

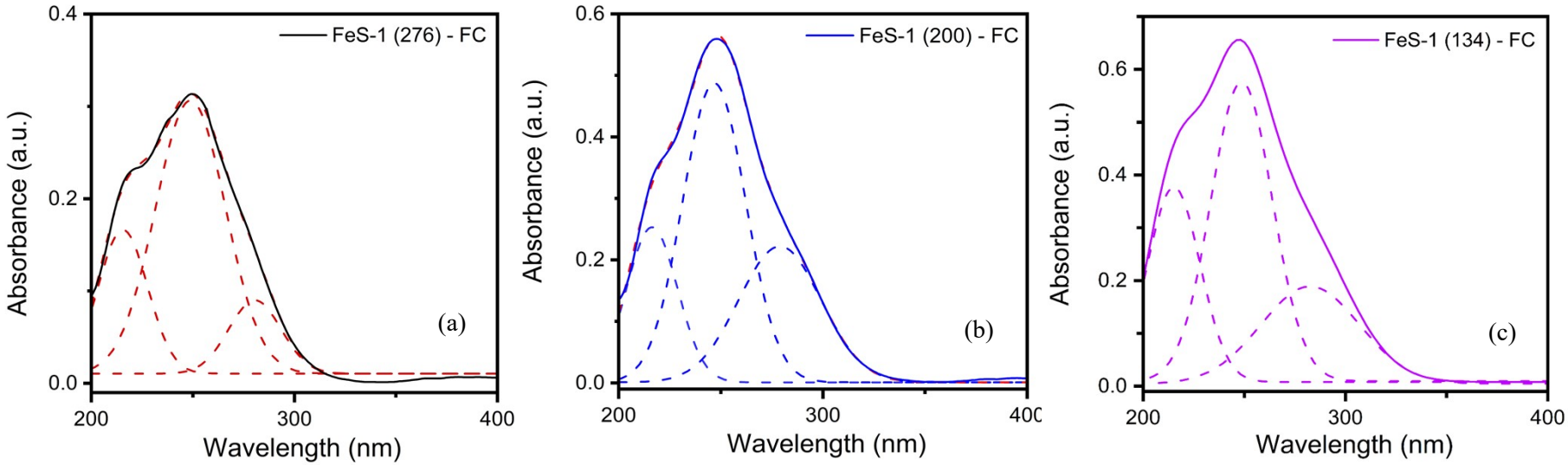

Figure S4. Deconvoluted DRUV-VIS spectra of various fresh (MFI) catalysts

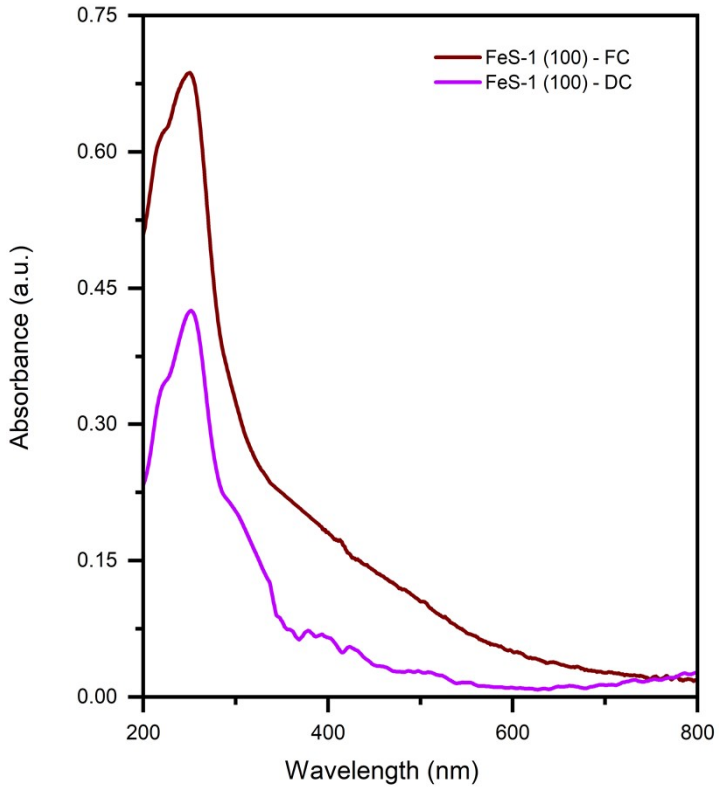

Figure S5. DRUV-VIS spectra of various FeS-1 catalysts.

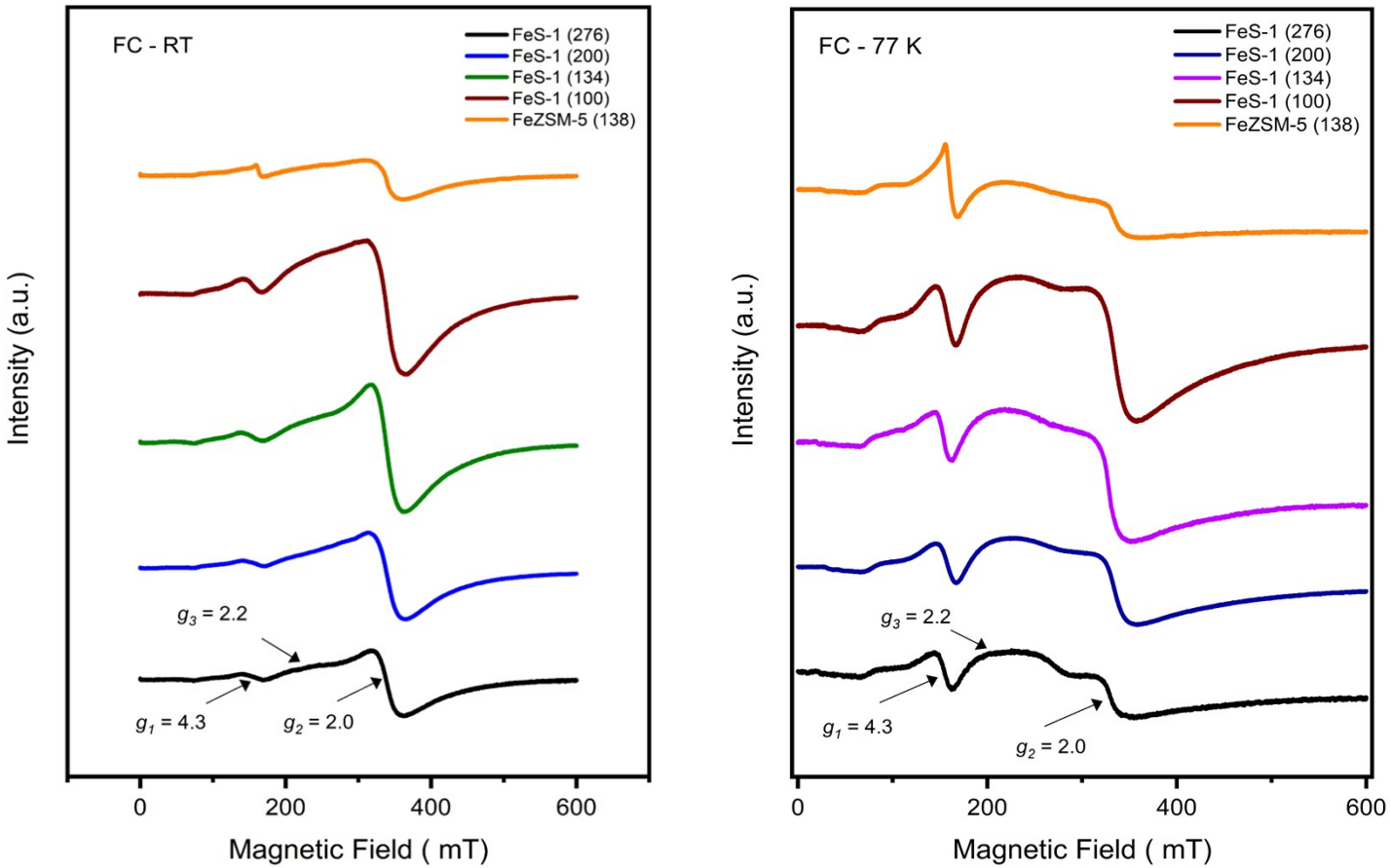

Figure S6. EPR data of various iron-containing MFI-framework structures.

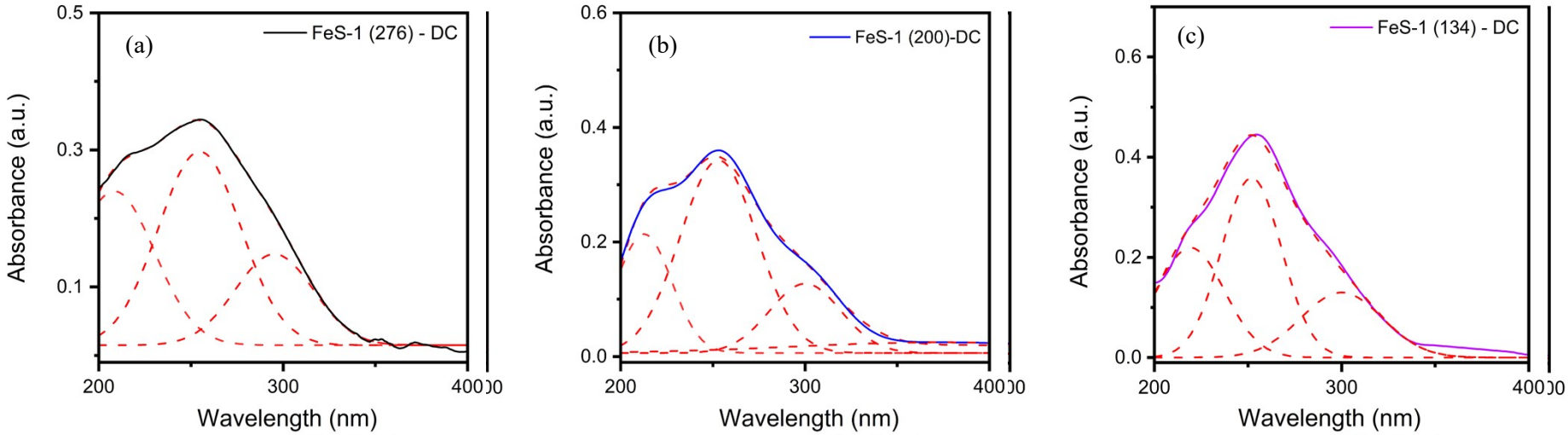

Figure S7. Deconvoluted DRUV-VIS spectra of various deferrated FeS-1 catalysts.

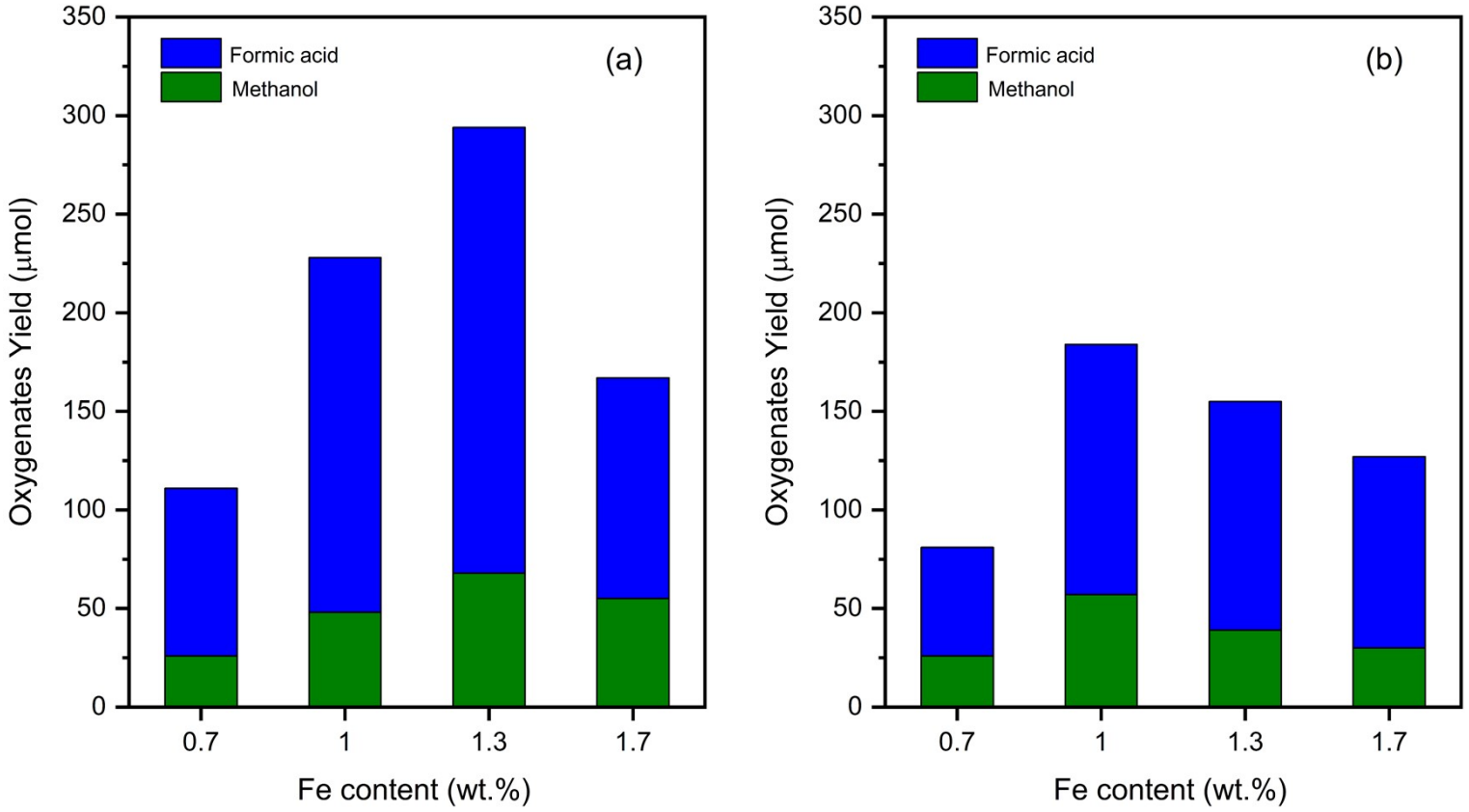

Figure S8. The catalytic activity of: (a) Fe-ZSM-5 (30) and (b) Fe-ZSM-5 (86).

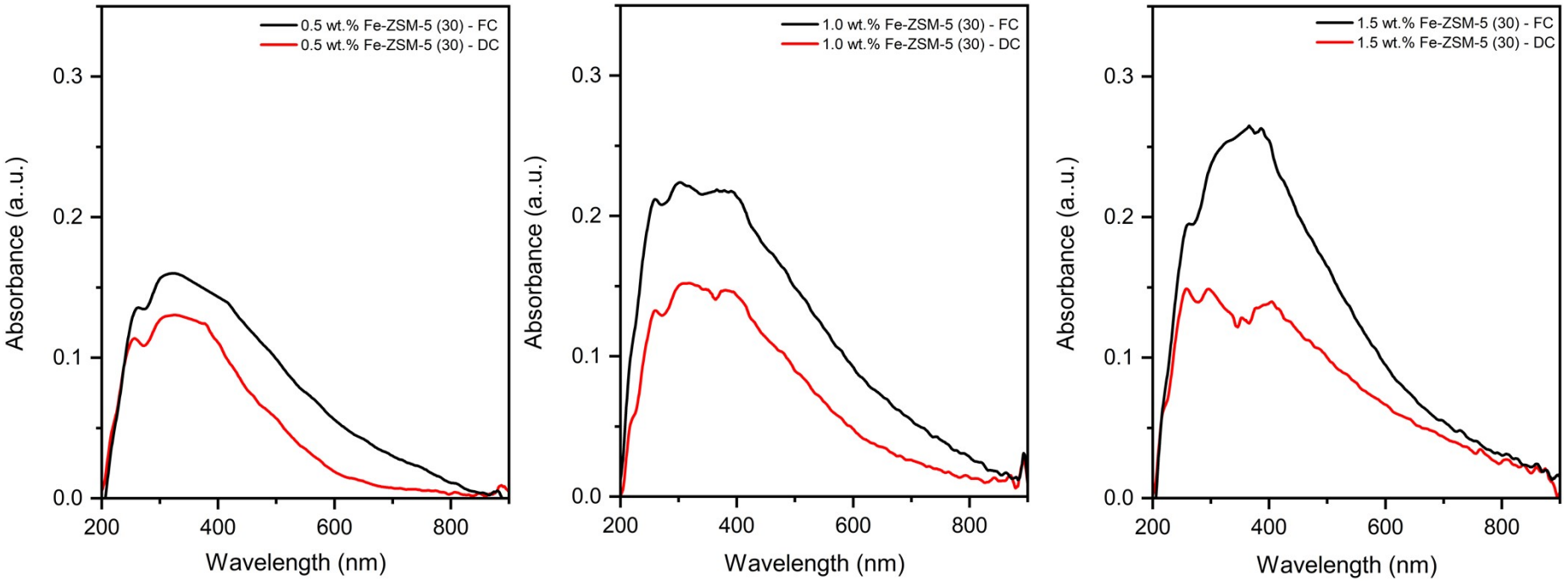
0.5 wt.% Fe-ZSM-5 (30) - FC
0.5 wt.% Fe-ZSM-5 (30) - DC
Absorbance (a..u.)
Wavelength (nm)
1.0 wt.% Fe-ZSM-5 (30) - FC
1.0 wt.% Fe-ZSM-5 (30) - DC
Absorbance (a..u.)
Wavelength (nm)
1.5 wt.% Fe-ZSM-5 (30) - FC
1.5 wt.% Fe-ZSM-5 (30) - DC
Absorbance (a..u.)
Wavelength (nm)

Figure S9. DRUV-VIS spectra of fresh deferrated Fe-MFI catalysts.

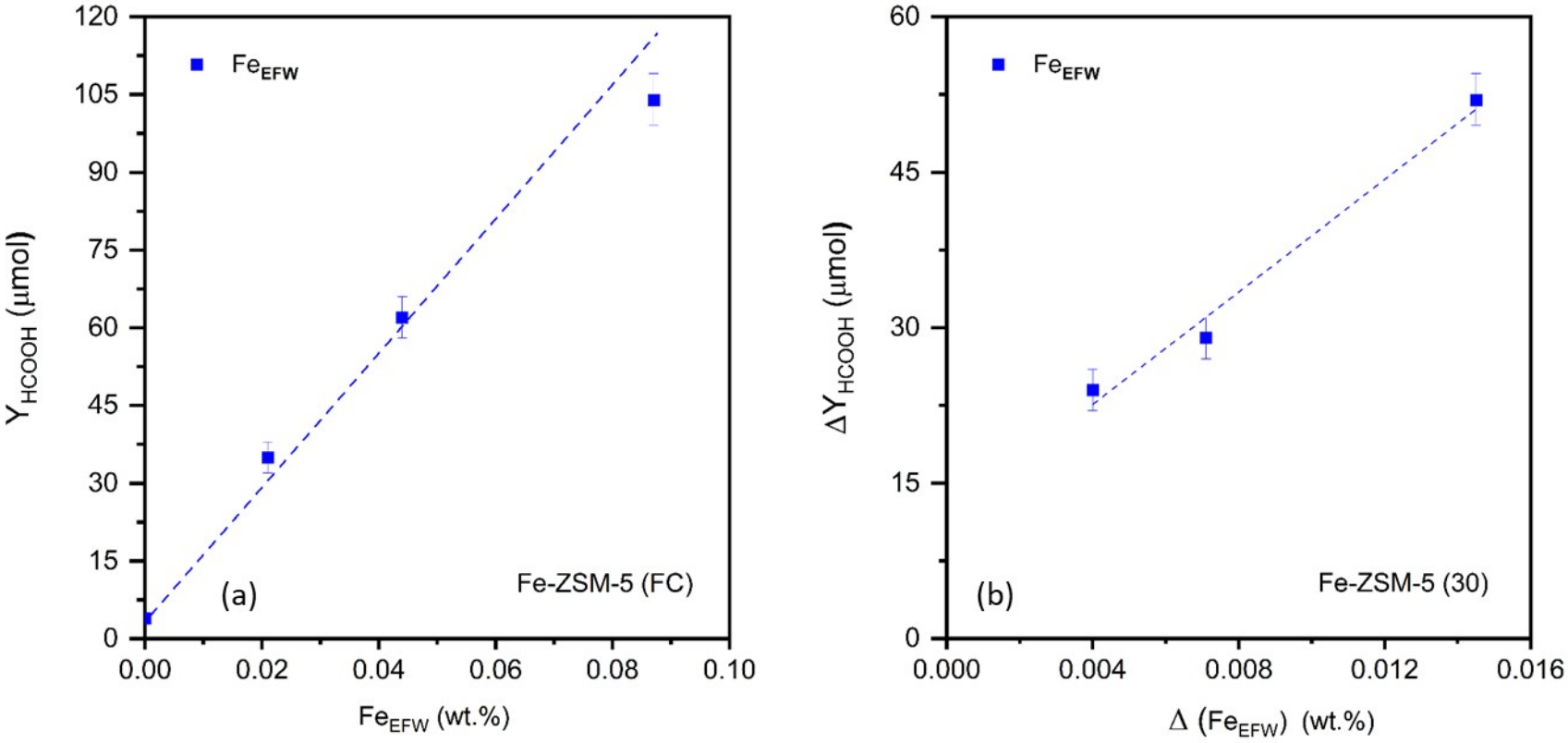

Figure S10. (a) A correlation between formic acid yield and extra-framework Fe content deduced from DRUV-VIS spectral data for Fe-ZSM-5 (30) – FC. (b) A correlation between formic acid loss (before and after deferration) and extra-framework iron decreased before and after deferration, deduced from DRUV-VIS.

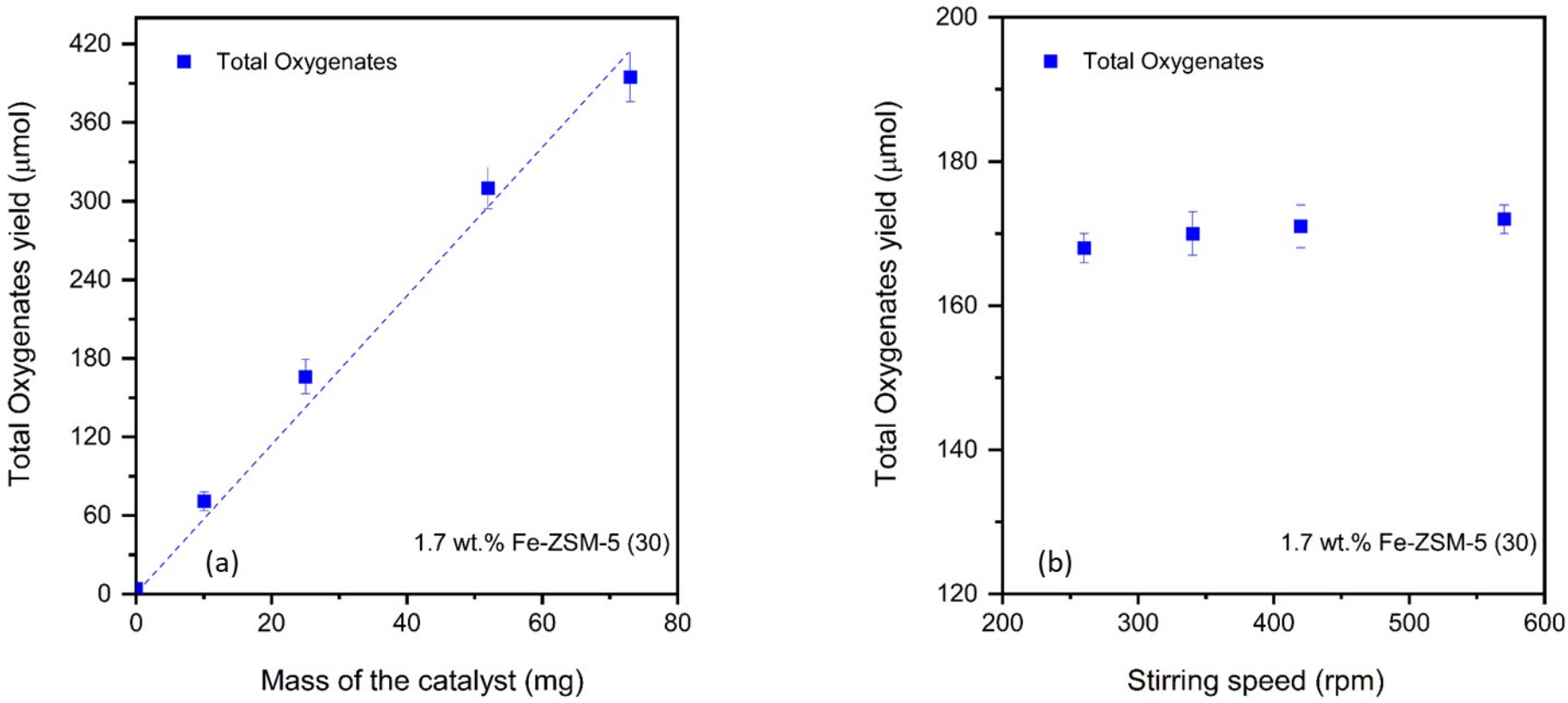

Figure S11. (a) A correlation between oxygenate yield and mass of the catalyst for Fe-ZSM-5 (30) – FC. Reaction conditions: Catalyst amount = 25 mg; $[H_2O_2]$ = 0.5 M; T = 50 °C; t = 30 min; Stirring speed = 570 rpm. (b) Effect of stirring speed on the total oxygenates productivity.