Supplementary Information

Zeolite Acidity Strongly Influences Hydrogen Peroxide Activation and Oxygenate Selectivity in the Partial Oxidation of Methane over M,Fe-MFI (M: Ga, Al, B) Zeolites

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Figure S13. Hydrogen peroxide consumption versus various catalysts. Conditions are similar for all the reactions: CH_4 Pressure: 443 psi, T: 55 °C, Amounts of catalyst: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min. (M, Al, PNa, Na)

Figure S14. Methane conversion/total oxygenated products, hydrogen peroxide consumption, and selectivity profiles as a function of partial pressure of methane over Ga,Fe-MFI(50). T: 55 °C, Weight $_{Catalyst}$: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min.

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Table S3. Catalytic studies of various (Ga/Al/B/Na),Fe-MFI zeolites for oxidation of methane under mild conditions. Conditions are similar for all the reactions: CH_4 Pressure: 443 psi, T: 55 °C,

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Table S4. Selectivity profile and turnover frequency for all the reactions in which (Ga/Al/B/Na),Fe-MFI zeolites were used. Conditions are similar for all the reactions: CH_4 Pressure: 443 psi, T: 55 °C, Weight $_{Catalyst}$: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min.

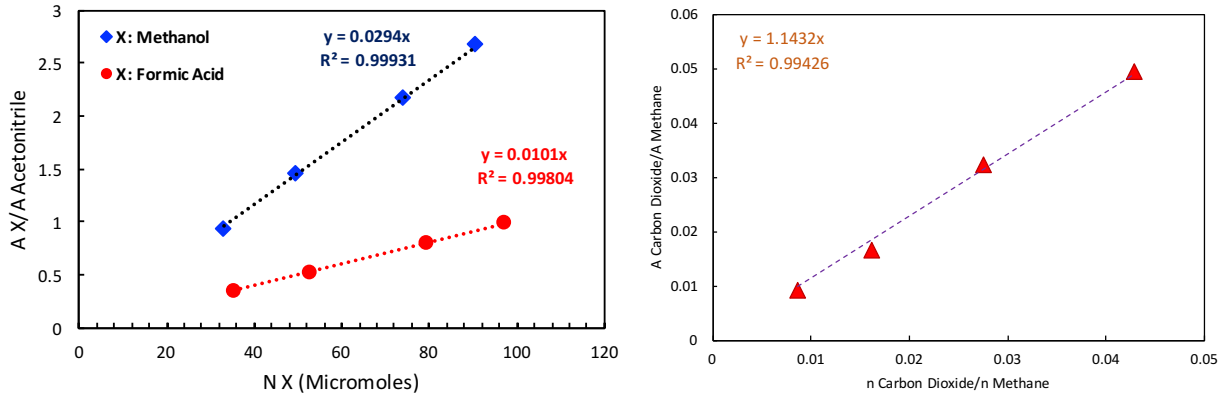


Figure S1. Left) Calibration curves of methanol/formic acid versus 0.25 vol% acetonitrile based on the ^{1}H-NMR spectrum. *(**Note:** Moles number was calculated based on the known amounts of methanol/formic acid inside the 10 mL of aqueous solution.)* Right) Calibration of carbon dioxide versus methane in gas chromatography using thermal conductivity as the detector.

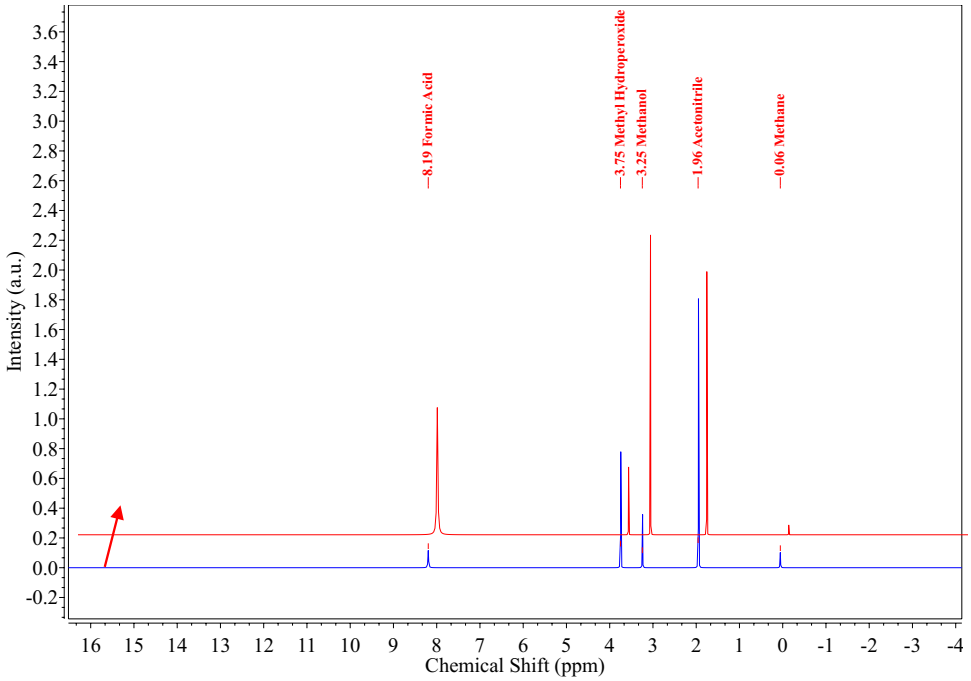


Figure S2. ^{1}H-NMR spectrum of organic oxygenates from direct oxidation of methane with H_2O_2 over B,Fe-MFI(200) (blue) and Ga,Fe-MFI(100) (red) after 30 min.

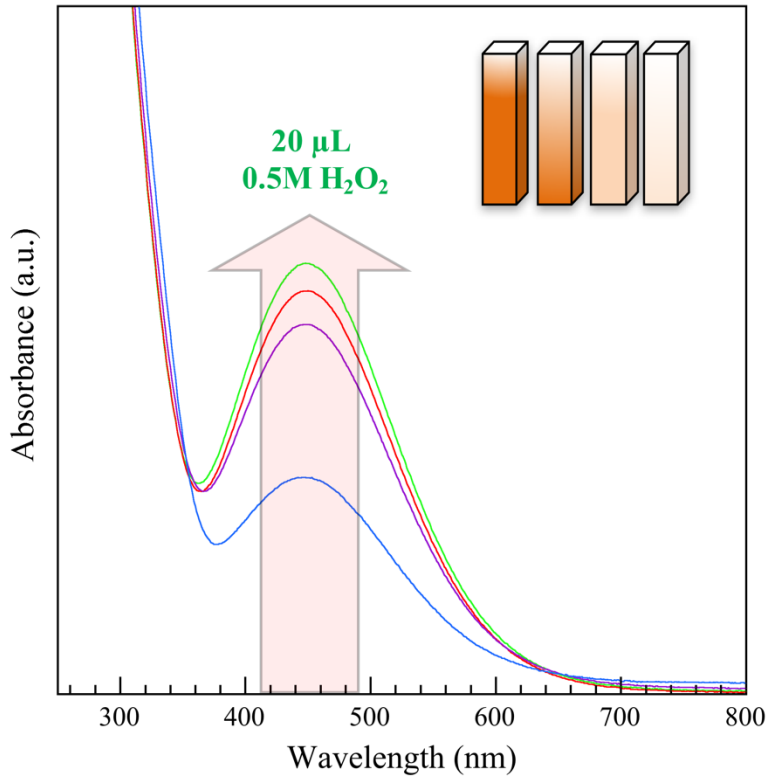


Figure S3. Ultraviolet-visible spectra of added certain amounts of hydrogen peroxide into 3 mL of V_2O_5 solution (0.002 M) *(Green spectrum: 20 µL of 0.5 M H_2O_2 added to vanadium pentoxide solution which shows a red-brownish color)*.

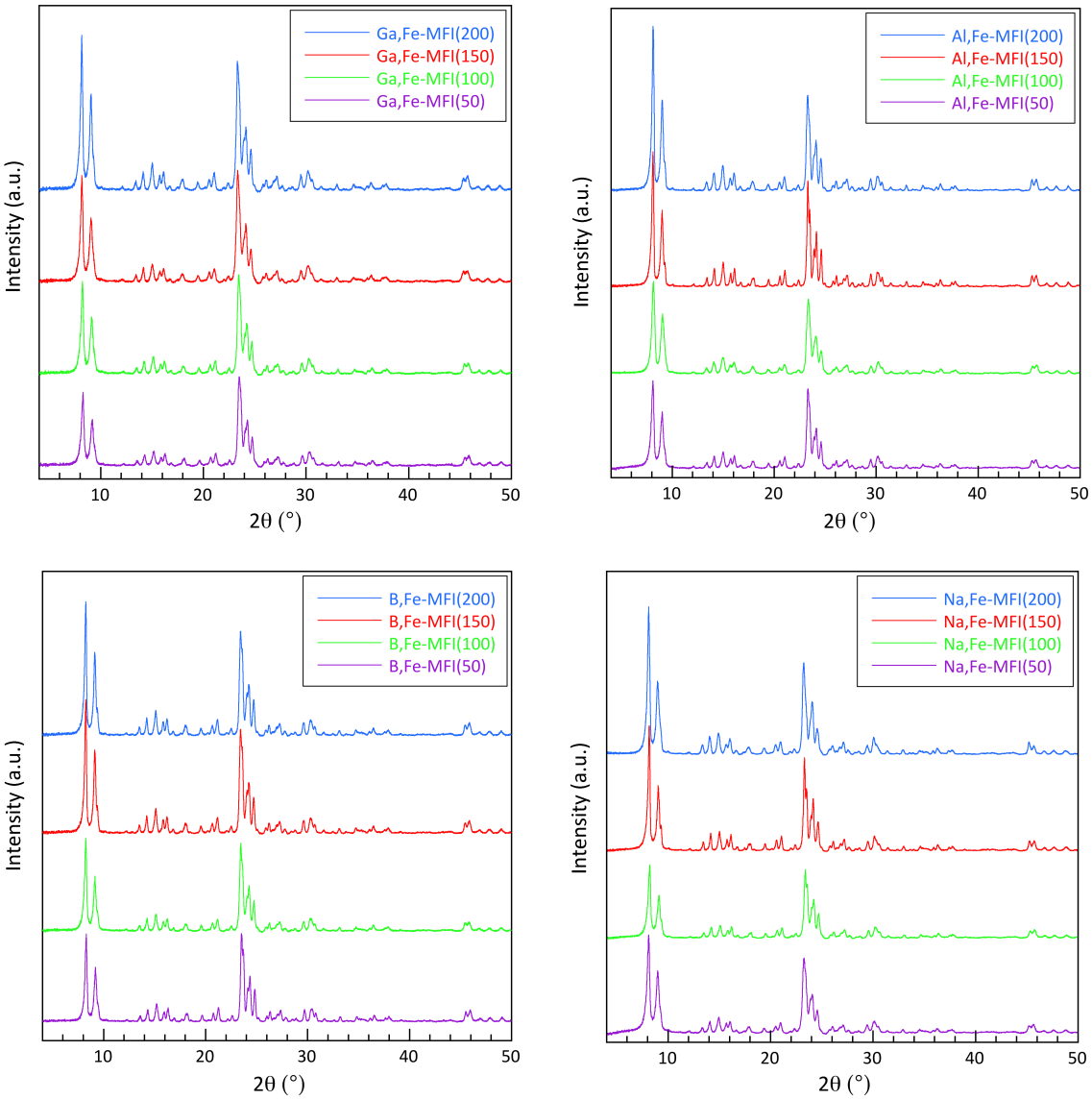


Figure S4. Powder X-ray diffraction patterns of calcined Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI zeolites in the range of 5° ≤ 2θ ≤ 50°.

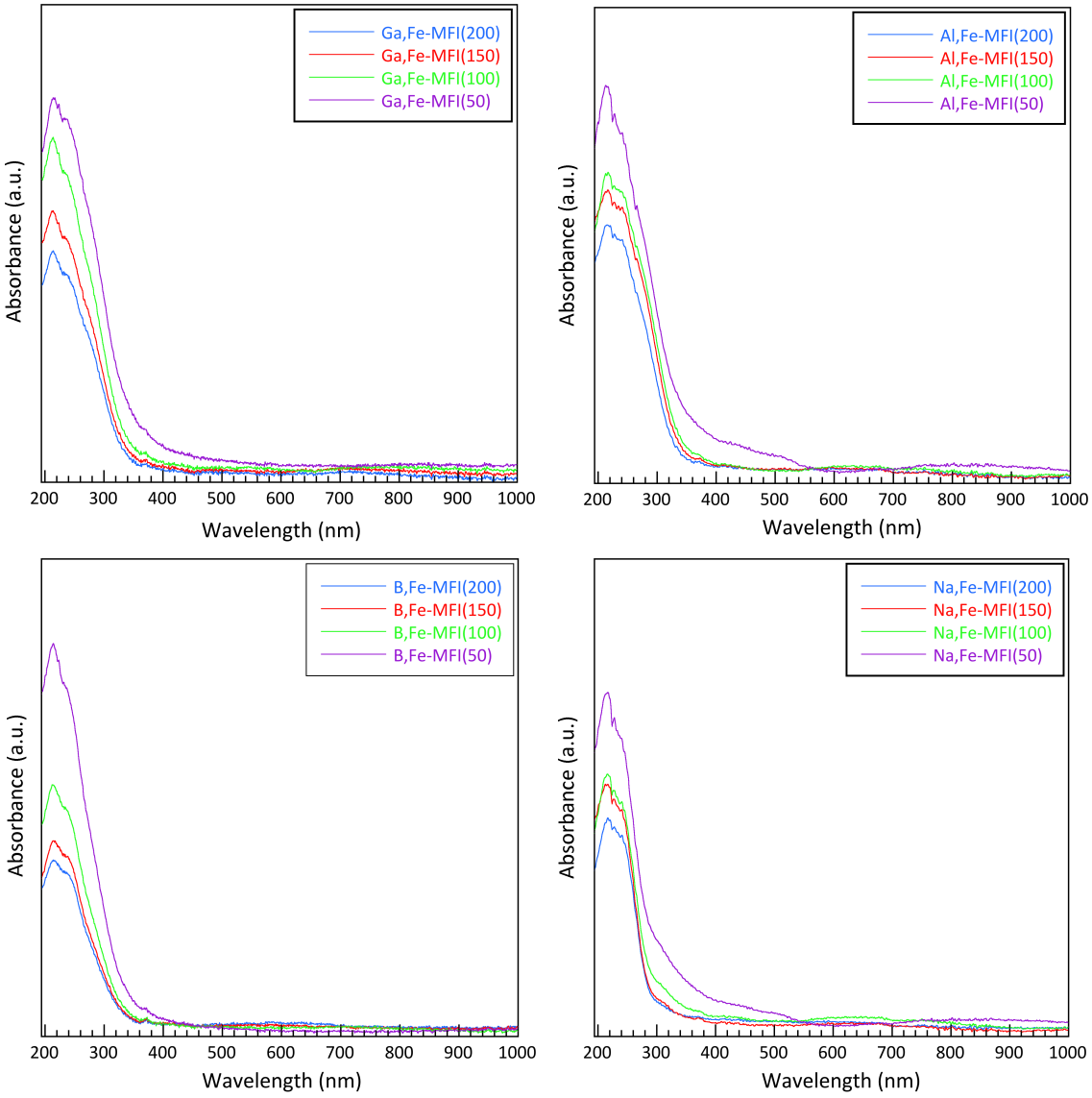


Figure S5. Ultraviolet-Visible spectra of calcined Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI zeolites in the range of 194-1000 nm under ambient conditions.

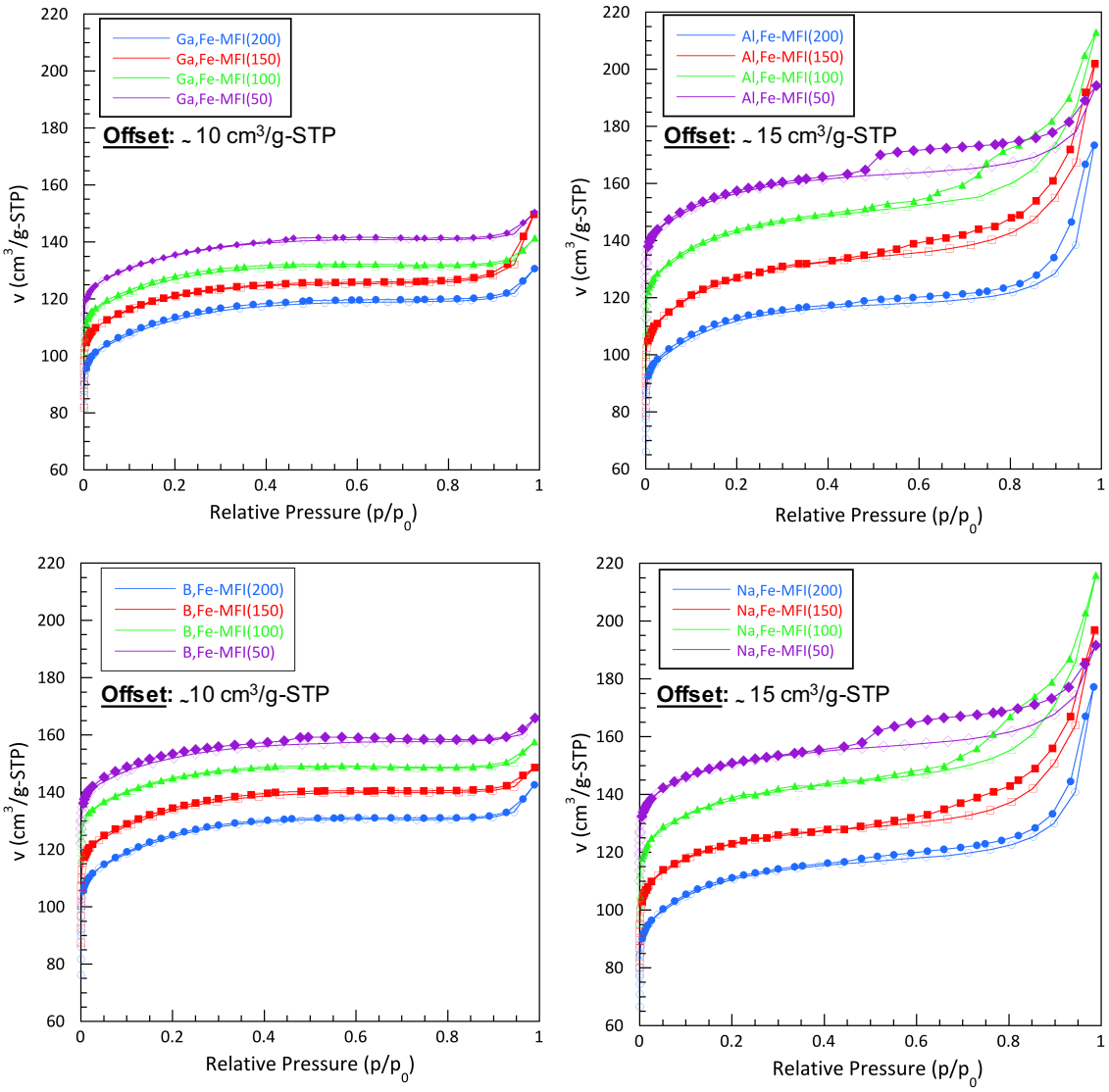


Figure S6. N_2 adsorption-desorption isotherms of outgassed Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI zeolites. (*60 < v (cm^3/g-STP) < 220*)

Sample Name	$V_{Micropore}$ (cm^3/g-STP)	V_{Total} (cm^3/g-STP)	S_{BET} (m^2/g)	$V_{Mesopore}$ (cm^3/g-STP)
Ga,Fe-MFI(200)	0.1404	0.2023	355	0.0619
Ga,Fe-MFI(150)	0.1344	0.2052	326	0.0708
Ga,Fe-MFI(100)	0.1324	0.1834	327	0.0510
Ga,Fe-MFI(50)	0.1294	0.1817	322	0.0523
Al,Fe-MFI(200)	0.1428	0.2783	352	0.1355
Al,Fe-MFI(150)	0.1382	0.2890	354	0.1508
Al,Fe-MFI(100)	0.1365	0.2832	357	0.1467
Al,Fe-MFI(50)	0.1337	0.2232	336	0.0895
B,Fe-MFI(200)	0.1570	0.2207	392	0.0637
B,Fe-MFI(150)	0.1499	0.2069	373	0.057
B,Fe-MFI(100)	0.1345	0.1821	328	0.0476
B,Fe-MFI(50)	0.1302	0.1793	320	0.0491
Na,Fe-MFI(200)	0.1394	0.2743	348	0.1349
Na,Fe-MFI(150)	0.1379	0.2809	339	0.143
Na,Fe-MFI(100)	0.1348	0.2870	341	0.1522
Na,Fe-MFI(50)	0.1310	0.2269	332	0.0959

Table S1. Physical properties of calcined Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI zeolites.

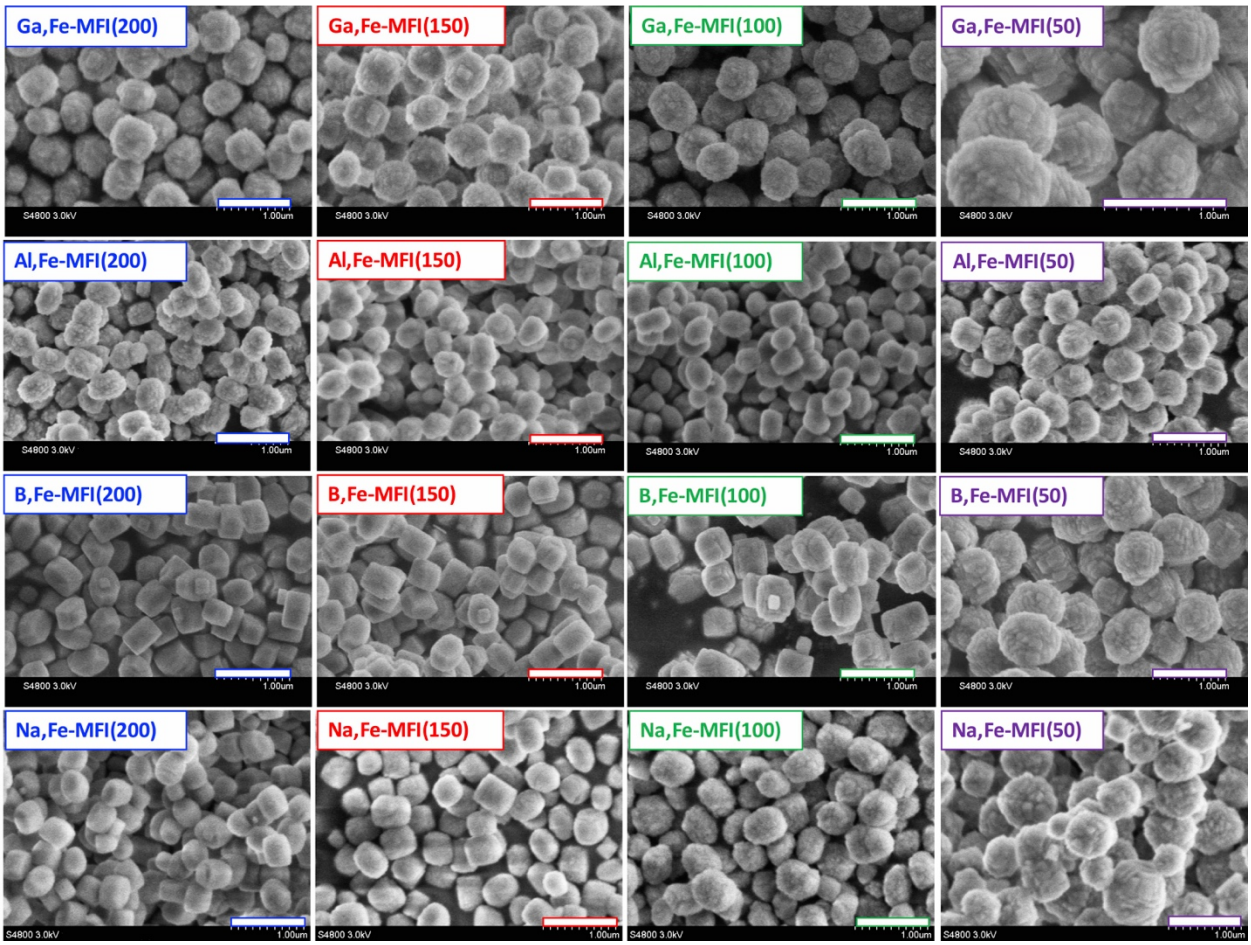


Figure S7. FE-SEM images of Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI zeolites. The scale bar in all images is 1 μm.

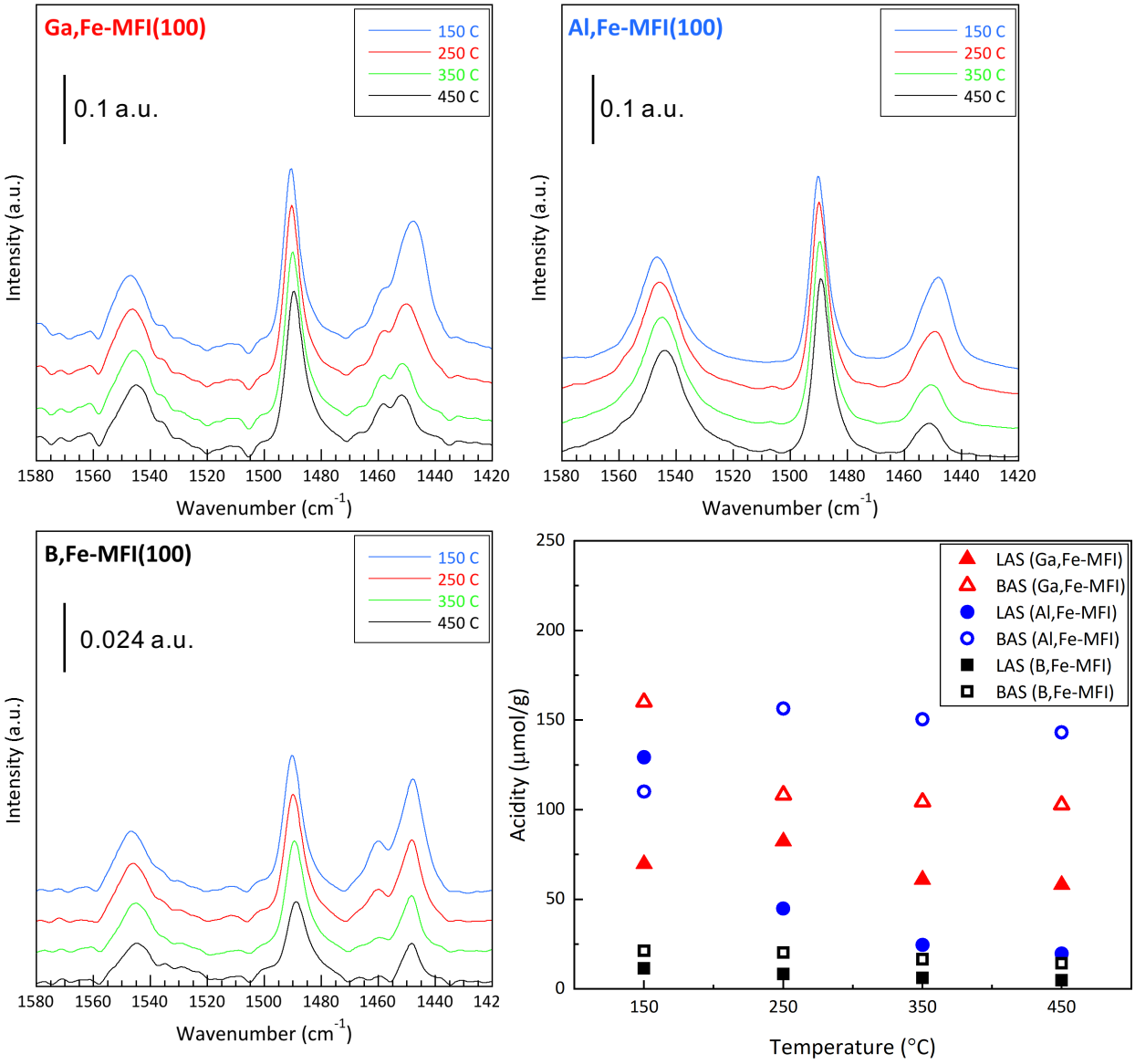
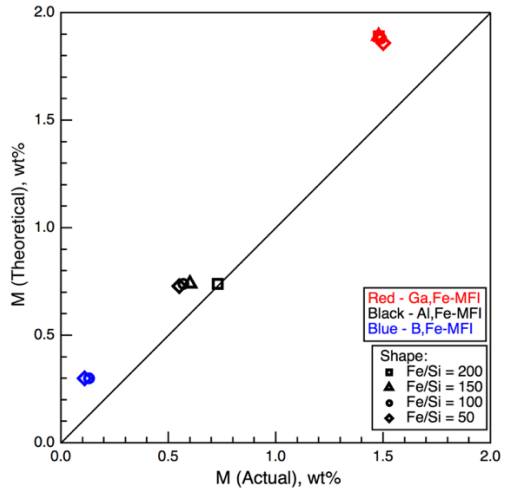


Figure S8. FT-IR spectra of pyridine adsorbed at different temperatures over M,Fe-MFI(100) zeolites as well as calculated concentration of Brönsted and Lewis acidities at different temperatures.

Sample Name	Theoretical wt%		Final wt% (EDX)			Uptake (%)	
	Fe (wt%)	Ga/Al/B (wt%)	Fe (wt%)	Ga/Al/B (wt%)	Na (wt%)	Fe (wt%)	Ga/Al/B (wt%)
Ga,Fe-MFI(200)	0.45	1.89	0.44	1.48	-	96.95	78.36
Ga,Fe-MFI(150)	0.60	1.89	0.56	1.48	-	92.68	78.48
Ga,Fe-MFI(100)	0.90	1.88	0.81	1.49	-	89.64	79.25
Ga,Fe-MFI(50)	1.79	1.86	1.63	1.5	-	91.01	80.50
Al,Fe-MFI(200)	0.46	0.74	0.45	0.73	-	98.01	98.72
Al,Fe-MFI(150)	0.61	0.74	0.55	0.6	-	89.98	81.26
Al,Fe-MFI(100)	0.91	0.74	0.75	0.57	-	82.05	77.44
Al,Fe-MFI(50)	1.81	0.73	1.41	0.55	-	77.83	75.40
B,Fe-MFI(200)	0.46	0.30	0.45	-	-	97.57	-
B,Fe-MFI(150)	0.61	0.30	0.60	-	-	97.72	-
B,Fe-MFI(100)	0.92	0.30	0.89	0.13	-	96.93	43.88
B,Fe-MFI(50)	1.82	0.29	1.65	0.11	-	90.68	37.47
Na,Fe-MFI(200)	0.46	0.74	0.44	0.71	0.61	95.83	96.01
Na,Fe-MFI(150)	0.61	0.74	0.53	0.67	0.6	86.70	90.74
Na,Fe-MFI(100)	0.91	0.74	0.77	0.56	0.66	84.23	76.08
Na,Fe-MFI(50)	1.81	0.73	1.39	0.55	0.86	76.73	75.40

Table S2. Theoretical wt%, actual wt%, and percent uptake of heteroatoms for all samples.



Plot of final wt% of M versus initial wt% of M for all catalysts. (M: Ga, Al, and B)

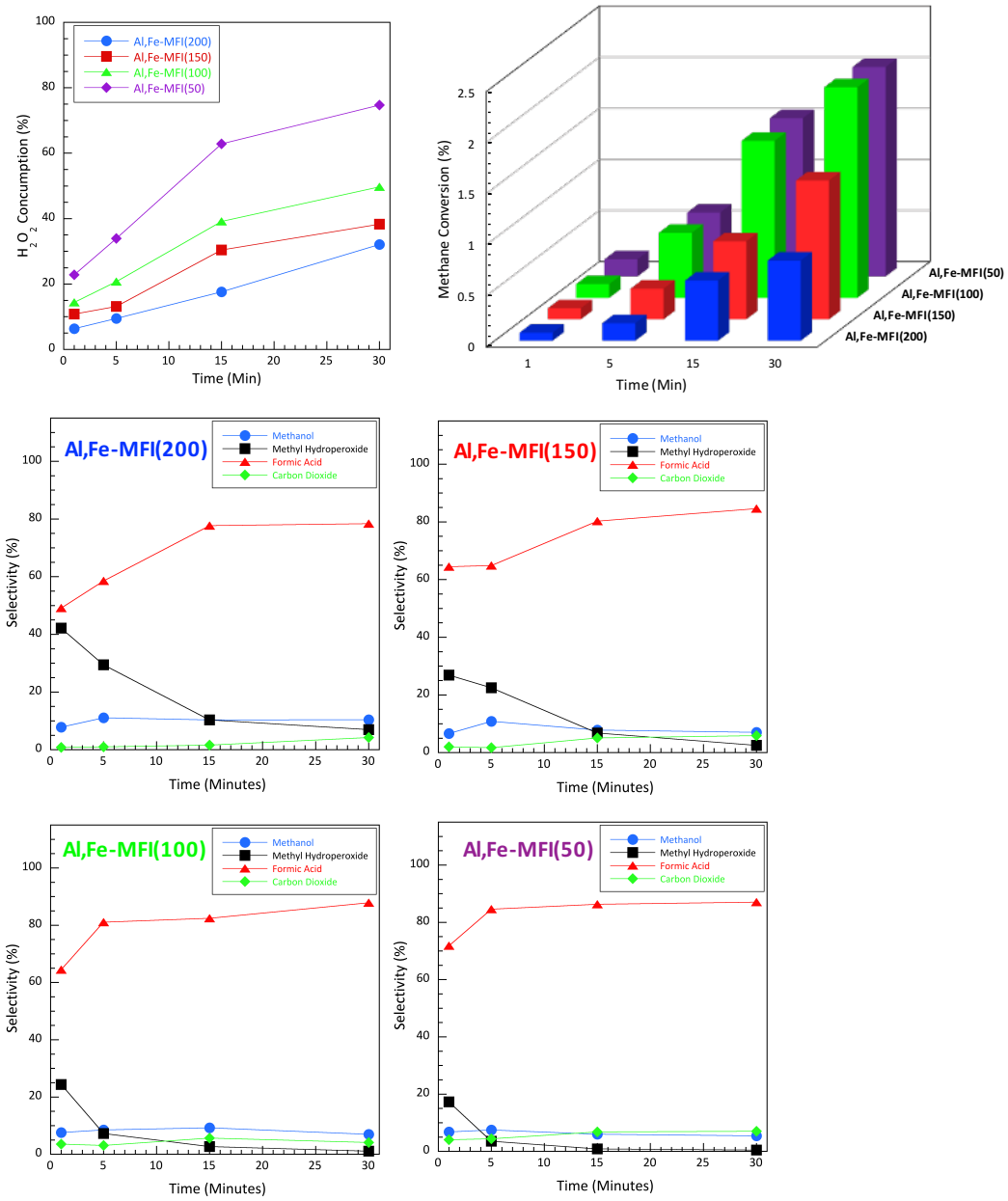
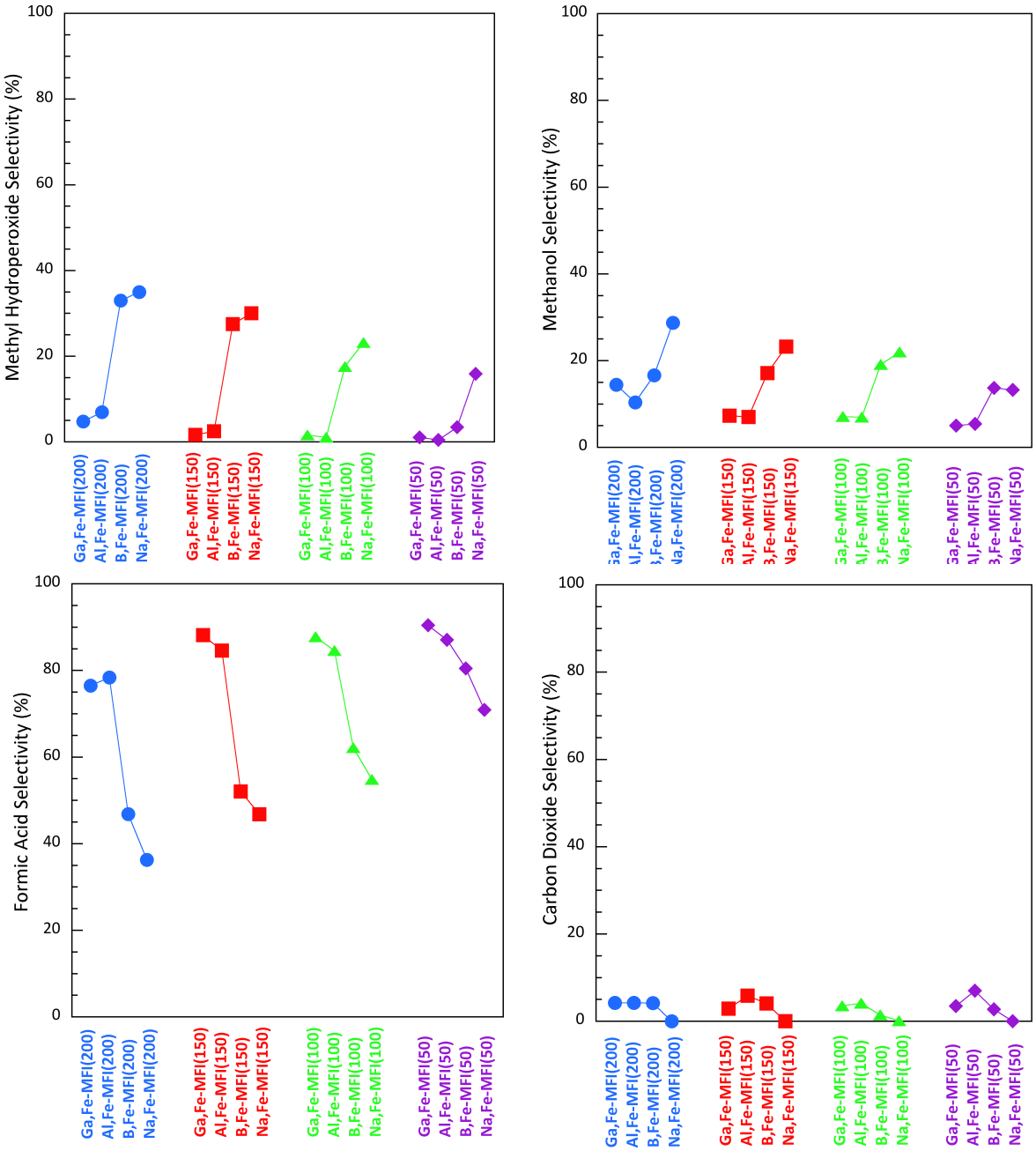


Figure S9. Hydrogen peroxide consumption (top left), methane conversion (top right), and selectivity profiles (bottom) versus time for a reaction in which Al,Fe-MFI zeolites were used as catalysts. Reaction conditions: CH_4 Pressure: 443 psi, T: 55 °C, Amounts of catalyst 28 mg, Concentration of H_2O_2: 0.5 M, Volume of used H_2O_2: 10 mL, 1500 rpm.



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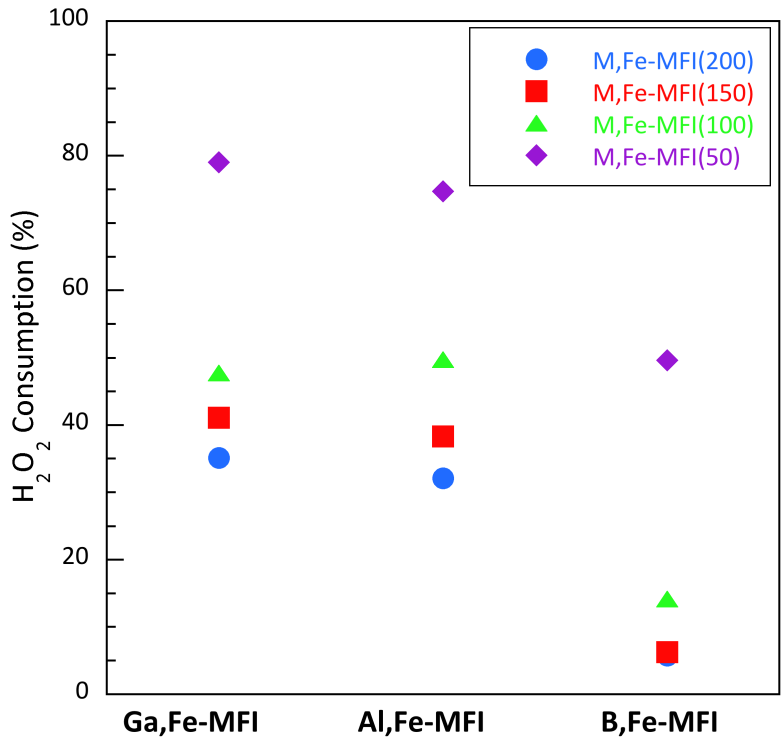

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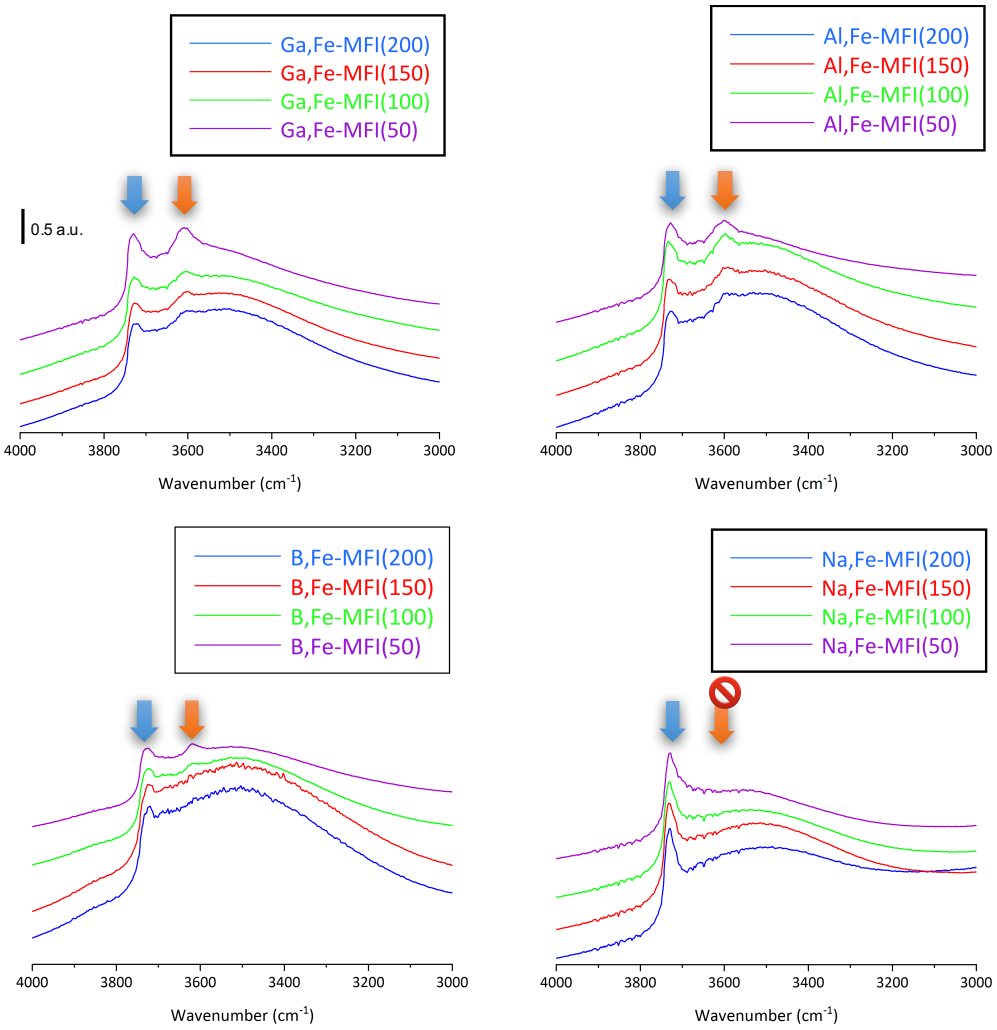
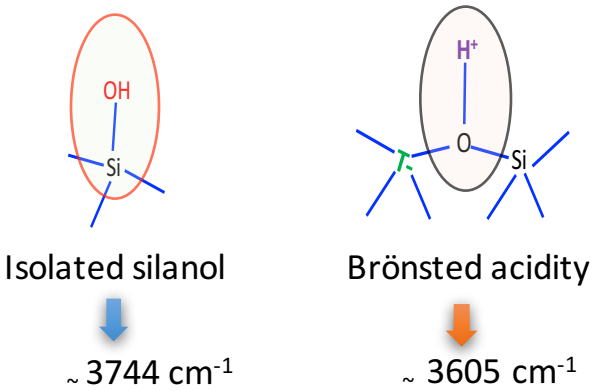
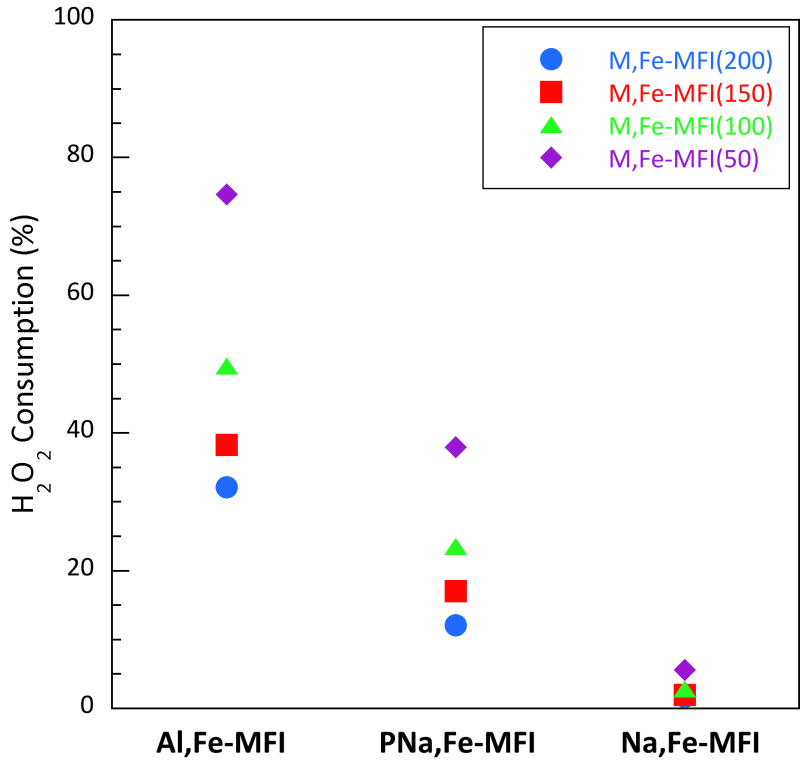


Figure S12. IR spectra of calcined Ga,Fe-MFI, Al,Fe-MFI, B,Fe-MFI, and Na,Fe-MFI materials under the vacuum (10^{-5} Torr) at 500 °C for 30 min in the range of 4000-3000 cm^{-1}. The indicator shows the Kubelka-Munk Function unit (a.u.).





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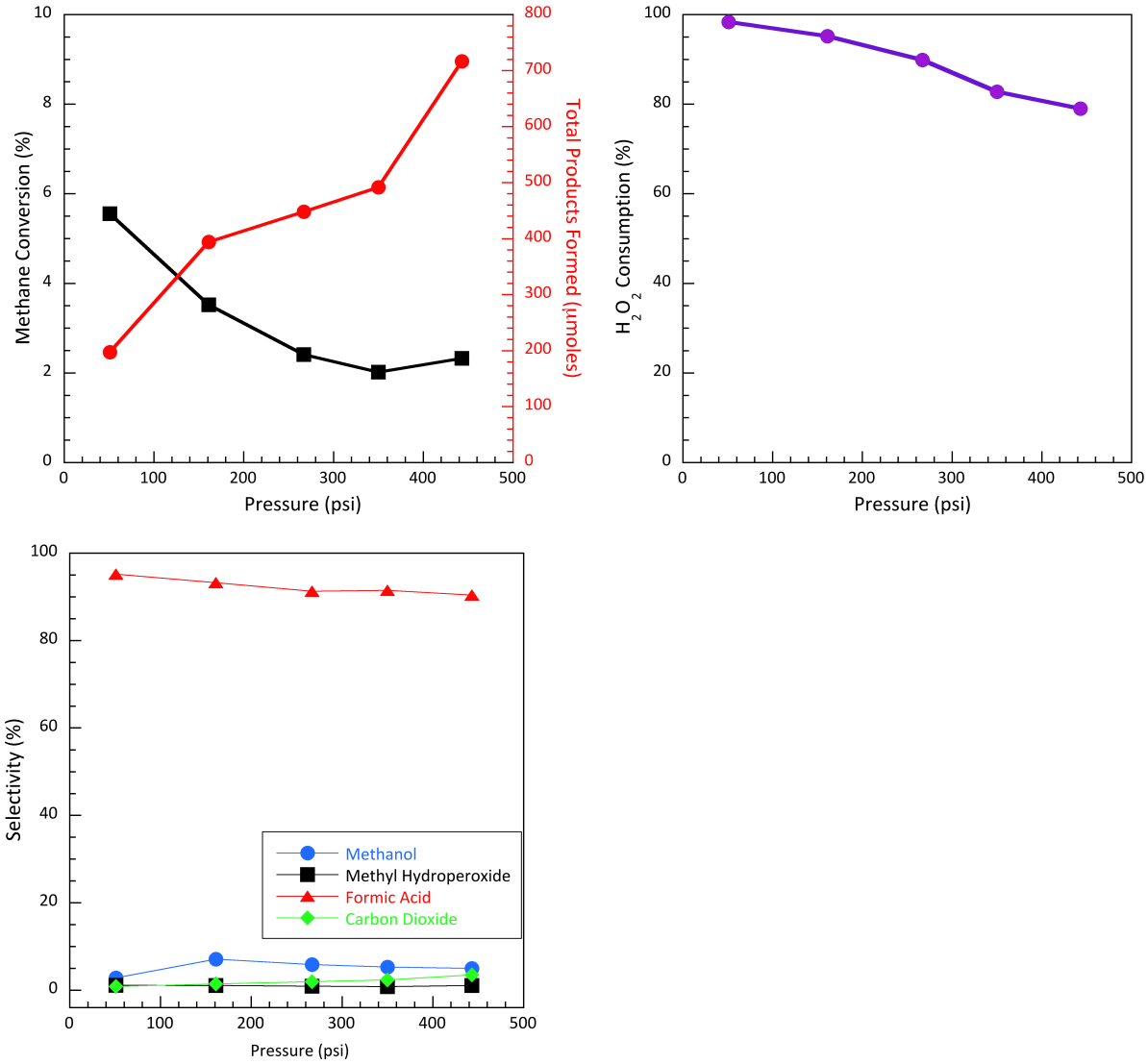

Figure S14. Methane conversion/total oxygenated products, hydrogen peroxide consumption, and selectivity profiles as a function of partial pressure of methane over Ga,Fe-MFI(50). T: 55 °C, Weight $_{Catalyst}$: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min.

Sample	CH_3OH (μmoles)	CH_3OOH (μmoles)	HCOOH (μmoles)	CO_2 (μmoles)	Total Products (μmoles)	Total Productivity (moles. Kg^{-1} $_{Catalyst.}$ h^{-1})
Ga,Fe-MFI(200)	39.52	13.08	209.19	11.65	273.44	19.53
Ga,Fe-MFI(150)	33.07	7.59	400.27	13.12	454.05	32.43
Ga,Fe-MFI(100)	44.59	10.07	549.62	22.02	626.31	44.74
Ga,Fe-MFI(50)	35.98	7.71	648.05	25.00	716.73	51.20
Al,Fe-MFI(200)	24.57	16.42	185.11	10.00	236.10	16.86
Al,Fe-MFI(150)	28.69	10.21	345.79	24.00	408.70	29.19
Al,Fe-MFI(100)	43.17	6.67	530.86	39.41	620.10	44.29
Al,Fe-MFI(50)	33.51	2.98	536.73	43.38	616.60	44.04
B,Fe-MFI(200)	8.14	16.13	22.89	1.70	48.87	3.49
B,Fe-MFI(150)	9.14	14.69	27.79	1.80	53.42	3.82
B,Fe-MFI(100)	26.04	23.95	84.77	1.61	136.36	9.74
B,Fe-MFI(50)	31.55	7.98	185.31	5.41	230.25	16.45
Na,Fe-MFI(200)	1.06	1.30	1.34	0.00	3.70	0.26
Na,Fe-MFI(150)	1.16	1.50	2.34	0.00	5.00	0.36
Na,Fe-MFI(100)	4.03	4.24	10.01	0.02	18.30	1.31
Na,Fe-MFI(50)	3.97	4.77	21.25	0.01	30.00	2.14

Table S3. Catalytic studies of various (Ga/Al/B/Na),Fe-MFI zeolites for oxidation of methane under mild conditions. Conditions are similar for all the reactions: CH_4 Pressure: 443 psi, T: 55 °C, Weight $_{Catalyst}$: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min.

Sample	S_{CH3OH} (%)	S_{CH3OOH} (%)	S_{HCOOH} (%)	S_{CO2} (%)	TOF (h^{-1})
Ga,Fe-MFI(200)	14.45	4.78	76.50	4.26	247.9
Ga,Fe-MFI(150)	7.28	1.67	88.16	2.89	317.7
Ga,Fe-MFI(100)	7.12	1.61	87.76	3.52	308.4
Ga,Fe-MFI(50)	5.02	1.08	90.42	3.49	175.4
Al,Fe-MFI(200)	10.41	6.95	78.40	4.24	209.3
Al,Fe-MFI(150)	7.02	2.50	84.61	5.87	296.4
Al,Fe-MFI(100)	6.96	1.08	85.61	6.36	329.8
Al,Fe-MFI(50)	5.44	0.48	87.05	7.04	174.4
B,Fe-MFI(200)	16.65	33.02	46.85	3.48	57.3
B,Fe-MFI(150)	17.10	27.50	52.03	3.37	38.7
B,Fe-MFI(100)	19.10	17.56	62.16	1.18	71.6
B,Fe-MFI(50)	13.70	3.47	80.48	2.35	58.9
Na,Fe-MFI(200)	28.73	35.00	36.28	0.00	3.4
Na,Fe-MFI(150)	23.23	30.00	46.77	0.00	3.8
Na,Fe-MFI(100)	22.00	23.15	54.72	0.13	9.5
Na,Fe-MFI(50)	13.23	15.90	70.84	0.03	8.6

Table S4. Selectivity profile and turnover frequency for all the reactions in which (Ga/Al/B/Na),Fe-MFI zeolites were used. Conditions are similar for all the reactions: CH_4 Pressure: 443 psi, T: 55 °C, Weight $_{Catalyst}$: 28 mg, Concentration of H_2O_2: 0.5 M, Volume of H_2O_2 Solution: 10 mL, 1500 rpm, t: 30 min.