Supporting Information:

DFT Study to Unravel the Catalytic Properties of M-Exchanged MFI, (M = Be, Co, Cu, Mg, Mn, Zn) for the Conversion of Methane and Carbon Dioxide to Acetic Acid.

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Table S1. Changes in the NBO charge of the carbon atom through CH_4 dissociation obtained with DFT.

	C in A	C in B	C in C
Be-MFI	-0.97	-0.98	-1.43
Co-MFI		-0.99	-1.29
Cu-MFI		-0.99	-1.04
Mg-MFI		-1.03	-1.49
Mn-MFI		-1.00	-1.39
Zn-MFI		-1.00	-1.39

Table S2. Changes in the NBO charge of the metal atom through CH_4 dissociation obtained with DFT.

	M in A	M in B	M in C
Be-MFI	1.319	1.315	1.307
Co-MFI	1.294	1.156	1.123
Cu-MFI	1.251	1.184	0.883
Mg-MFI	1.614	1.525	1.502
Mn-MFI	1.387	1.173	1.244
Zn-MFI	1.431	1.326	1.325

Table S3. Energy contributions in kcal/mol to CH_4 adsorption energies obtained with ONIOM.

	DFT	Stretching, bending, and torsion	Disp.	Total
Be-MFI	-0.71	-0.11	-7.86	-8.69
Co-MFI	-0.44	-0.23	-8.26	-8.93
Cu-MFI	-2.65	-0.17	-8.20	-11.02
Mg-MFI	-4.96	-0.30	-8.66	-13.92
Mn-MFI	-5.12	-0.37	-8.28	-13.77
Zn-MFI	-4.26	-0.40	-8.40	-13.06

Table S4. Energy contributions in kcal/mol to CH_4 dissociation energies obtained with ONIOM.

	DFT	Stretching, bending, and torsion	Disp.	Total
Be-MFI	22.18	-2.01	-0.18	19.98
Co-MFI	21.86	-2.24	0.20	19.82
Cu-MFI	10.36	-2.71	-0.09	7.57
Mg-MFI	40.96	-1.96	0.44	39.43
Mn-MFI	31.04	-1.36	-0.39	29.30
Zn-MFI	10.74	-1.72	-0.17	8.85

Table S5. Energy contributions in kcal/mol to the TS energies of CH_4 dissociation obtained with ONIOM.

	DFT	Stretching, bending, and torsion	VDW	Total
Cu-MFI	24.30725	-2.44235	0.673359	22.53826
Zn-MFI	30.11197	-1.94533	0.563884	28.73053

Table S6. Geometric parameters of the TS for CH_4 dissociation on Cu-MFI obtained with ONIOM and with the DFT cluster.

Cu-MFI	DFT	ONIOM
d_{M-C} (Å)	2.11	2.02
d_{M-O4} (Å)	2.04	3.44
d_{M-O2} (Å)	2.28	1.92
d_{M-O5} (Å)	3.33	1.92
Mulliken Charge	-0.16	0.56

Table S7. Geometric parameters of the TS for CH_4 dissociation on Zn-MFI obtained with ONIOM and with the DFT cluster.

Zn-MFI	DFT	ONIOM
d_{M-C} (Å)	2.10	2.04
d_{M-O4} (Å)	2.32	2.00
d_{M-O2} (Å)	2.08	3.35
d_{M-O5} (Å)	3.25	1.95
Mulliken Charge	0.21	0.38

The coordinates of all stable intermediates and transition states with its respective IRC paths are in the S_I.zip file.