Supplementary Information

Propane dehydrogenation on extra-framework and framework-embedded metal site within ZSM-5 zeolite from first-principles microkinetic simulations

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Table S1. The ZPE-corrected energies of PDH on three kinds of EF-MOH^+ and EF-M^{2+} sites at 0 K. Unit: kJ/mol.

		Concerted pathway							Stepwise pathway								
		IS	M1	TS1	M2	TS2	M3	FS	IS	M1	TS1	M2	TS2	M3	M4	TS3	FS
EF	CuOH	0	-57	19	-55	125	-8	100	0	-57	19	-55	26	24	78	144	100
	NiOH	0	-61	45	-15	144	-16	100	0	-61	45	-15	58	-3	49	132	100
	CoOH	0	-55	51	-18	146	-28	100	0	-55	51	-18	91	38	90	160	100
	Cu	0	-60	46	32	149	9	100	0	-60	46	32	76	61	154	166	100
	Ni	0	-74	61	56	145	-33	100	0	-74	61	56	101	-5	164	165	100
	Co	0	-66	72	68	148	-31	100	0	-66	72	68	136	67	182	199	100

Table S2. The ZPE-corrected energies of PDH on three kinds of FE-MOH^+ and FE-M^{2+} sites at 0 K. Unit: kJ/mol.

		Concerted pathway							Stepwise pathway								
		IS	M1	TS1	M2	TS2	M3	FS	IS	M1	TS1	M2	TS2	M3	M4	TS3	FS
FE	CuOH	0	-54	-1	-28	144	48	100	0	-54	-1	-28	51	50	92	129	100
	NiOH	0	-57	77	9	170	38	100	0	-57	77	9	90	83	87	129	100
	CoOH	0	-48	109	35	194	56	100	0	-48	109	35	131	100	146	184	100
	Cu	0	-56	9	-38	125	-12	100	0	-56	9	-38	12	-1	108	172	100
	Ni	0	-61	57	7	154	36	100	0	-61	57	7	46	21	133	166	100
	Co	0	-56	87	53	165	22	100	0	-56	87	53	111	49	154	191	100

Table S3. Reaction energies (ΔE) and energy barriers (E_a) at 0 K, forward rate constants (k_{fwd}) and backward rate constants (k_{bkd}), as well as the degree of rate control (*DRC*) at 853 K of the involved elementary steps of PDH reaction on four types of metal sites in ZSM-5.

	Type	Elementary step	ΔE / kJ/mol	E_a / kJ/mol	k_{fwd} / s^{-1}	k_{bkd} / s^{-1}	*DRC*
EF-CuOH	**TS1**	C_3H_8*→ C_3H_7H*	2	76	3.84E+05	8.29E+06	8.85E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	47	180	1.53E+01	1.29E+01	6.18E-04
	TS2/S	C_3H_7H*→C_3H_6HH*	79	81	6.32E+07	3.89E+10	1.17E-01
	TS3	HH*→ H_2*	15	66	3.35E+08	3.53E+05	1.30E-03
EF-NiOH	**TS1**	C_3H_8*→ C_3H_7H*	46	106	6.31E+03	6.93E+07	1.11E-02
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-1	159	8.46E+01	8.61E-02	1.08E-04
	TS2/S	C_3H_7H*→C_3H_6HH*	12	73	7.77E+05	3.74E+04	9.89E-01
	TS3	HH*→ H_2*	41	83	3.75E+07	1.40E+06	2.71E-08
EF-CoOH	**TS1**	C_3H_8*→ C_3H_7H*	37	106	5.89E+03	1.93E+07	-5.80E-03
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-10	164	9.71E+01	2.87E-02	-2.12E-03
	TS2/S	C_3H_7H*→C_3H_6HH*	56	109	3.68E+04	8.29E+05	9.90E-01
	TS3	HH*→ H_2*	4	70	2.17E+08	4.40E+04	-1.11E-02
EF-Cu	**TS1**	C_3H_8*→ C_3H_7H*	92	106	8.14E+03	4.83E+10	1.35E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-23	117	1.60E+04	5.87E+00	1.84E-06
	TS2/S	C_3H_7H*→C_3H_6HH*	29	44	8.16E+09	1.51E+12	7.97E-01
	TS3	HH*→ H_2*	-64	12	8.61E+10	8.13E+05	2.24E-10
EF-Ni	**TS1**	C_3H_8*→ C_3H_7H*	130	135	1.25E+02	1.71E+11	1.02E-02
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-89	91	3.49E+05	1.23E-02	4.79E-03
	TS2/S	C_3H_7H*→C_3H_6HH*	-61	45	6.07E+08	3.46E+05	1.00E+00
	TS3	HH*→ H_2*	-77	1	4.35E+11	7.00E+05	1.11E-02
EF-Co	**TS1**	C_3H_8*→ C_3H_7H*	133	138	8.77E+01	1.88E+11	6.34E-03
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-99	80	8.60E+05	7.68E-03	4.04E-02
	TS2/S	C_3H_7H*→C_3H_6HH*	5	68	2.29E+07	6.09E+07	9.68E-01
	TS3	HH*→ H_2*	-95	17	4.13E+10	4.75E+03	1.11E-02
FE-CuOH	**TS1**	C_3H_8*→ C_3H_7H*	26	53	2.92E+07	9.22E+09	7.26E-03
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	76	172	2.21E+03	2.45E+04	3.25E-05
	TS2/S	C_3H_7H*→C_3H_6HH*	78	79	6.76E+07	6.26E+10	9.89E-01
	TS3	HH*→ H_2*	-9	37	4.44E+09	5.66E+05	3.87E-08
FE-NiOH	**TS1**	C_3H_8*→ C_3H_7H*	66	134	3.80E+02	2.96E+07	9.21E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	29	161	5.78E+02	9.09E+00	1.31E-07
	TS2/S	C_3H_7H*→C_3H_6HH*	74	81	3.49E+08	1.37E+11	7.81E-02
	TS3	HH*→ H_2*	1	42	2.07E+09	1.15E+06	1.97E-10
FE-CoOH	**TS1**	C_3H_8*→ C_3H_7H*	84	157	1.15E+01	1.19E+07	8.68E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	21	159	2.80E+02	1.35E+00	4.75E-07
	TS2/S	C_3H_7H*→C_3H_6HH*	65	96	7.79E+07	8.30E+09	1.32E-01
	TS3	HH*→ H_2*	-57	38	3.88E+09	6.29E+02	9.53E-13

FE-Cu	**TS1**	C_3H_8*→ C_3H_7H*	18	65	2.57E+07	1.27E+09	4.61E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	26	163	3.32E+02	3.45E-01	-2.31E-03
	TS2/S	C_3H_7H*→C_3H_6HH*	37	50	1.13E+09	3.64E+11	5.20E-01
	TS3	HH*→ H_2*	-17	64	2.33E+08	2.97E+04	-5.50E-03
FE-Ni	**TS1**	C_3H_8*→ C_3H_7H*	68	118	1.61E+04	8.22E+08	6.27E-01
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	29	147	1.84E+03	3.72E+00	4.96E-07
	TS2/S	C_3H_7H*→C_3H_6HH*	14	39	1.39E+09	9.30E+10	3.71E-01
	TS3	HH*→ H_2*	-41	33	1.99E+10	7.70E+04	8.55E-10
FE-Co	**TS1**	C_3H_8*→ C_3H_7H*	109	143	4.50E+02	8.30E+09	7.36E-03
	TS2/C	C_3H_7H*→ $C_3H_6H_2$*	-31	112	1.64E+05	6.14E-02	-4.50E-03
	TS2/S	C_3H_7H*→C_3H_6HH*	-4	58	1.29E+08	4.37E+08	9.76E-01
	TS3	HH*→ H_2*	-63	37	1.19E+10	2.21E+03	-1.66E-02

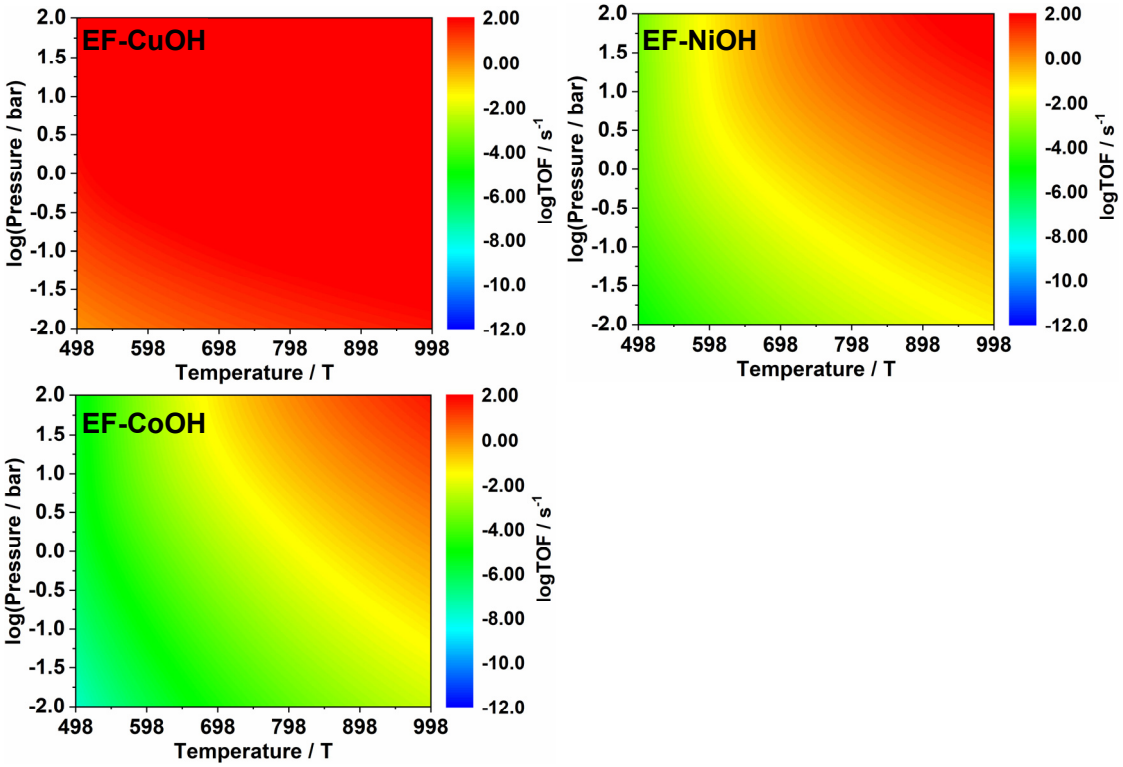

Figure S1. Activity plots of PDH on three kinds of EF-MOH⁺ sites as a function of temperature and pressure.

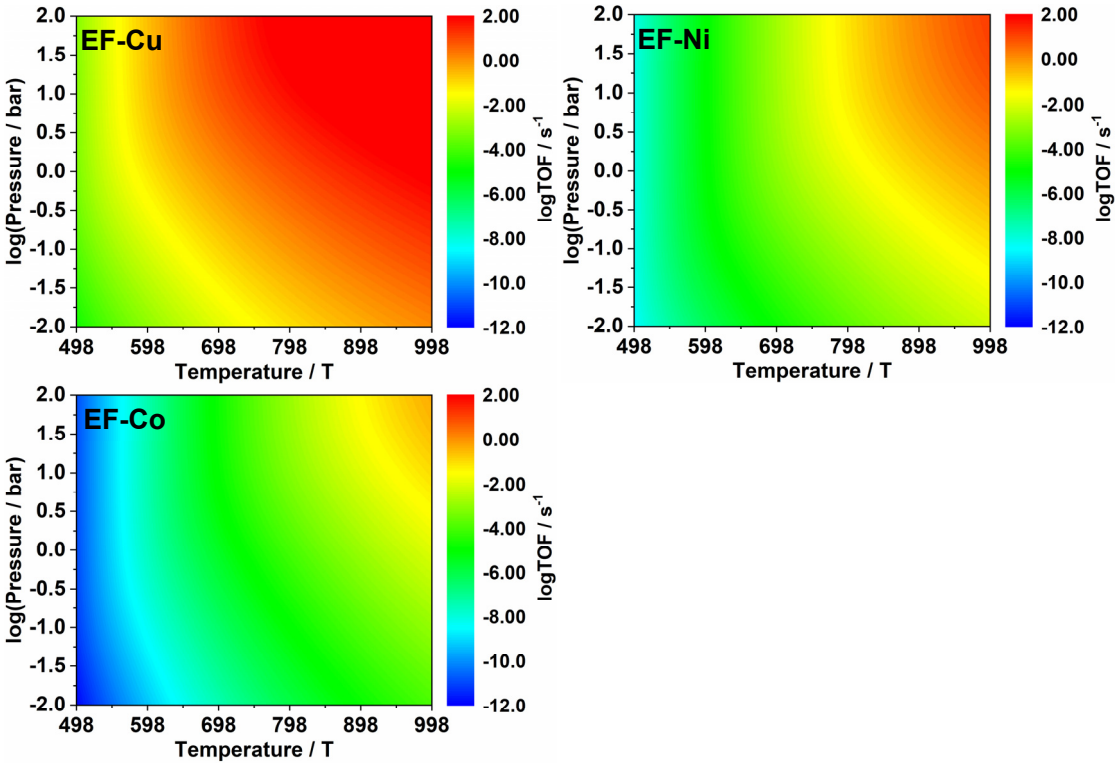

Figure S2. Activity plots of PDH on three kinds of EF-M^{2+} sites as a function of temperature and pressure.

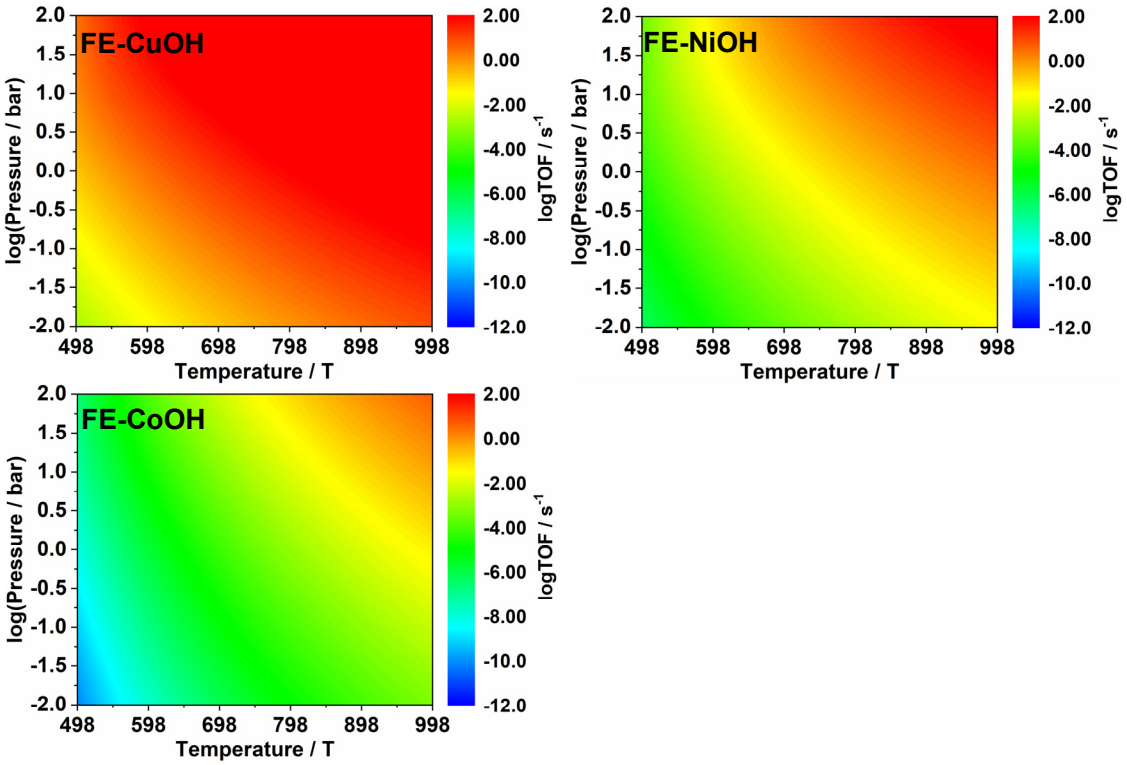

Figure S3. Activity plots of PDH on three kinds of FE-MOH$^+$ sites as a function of temperature and pressure.

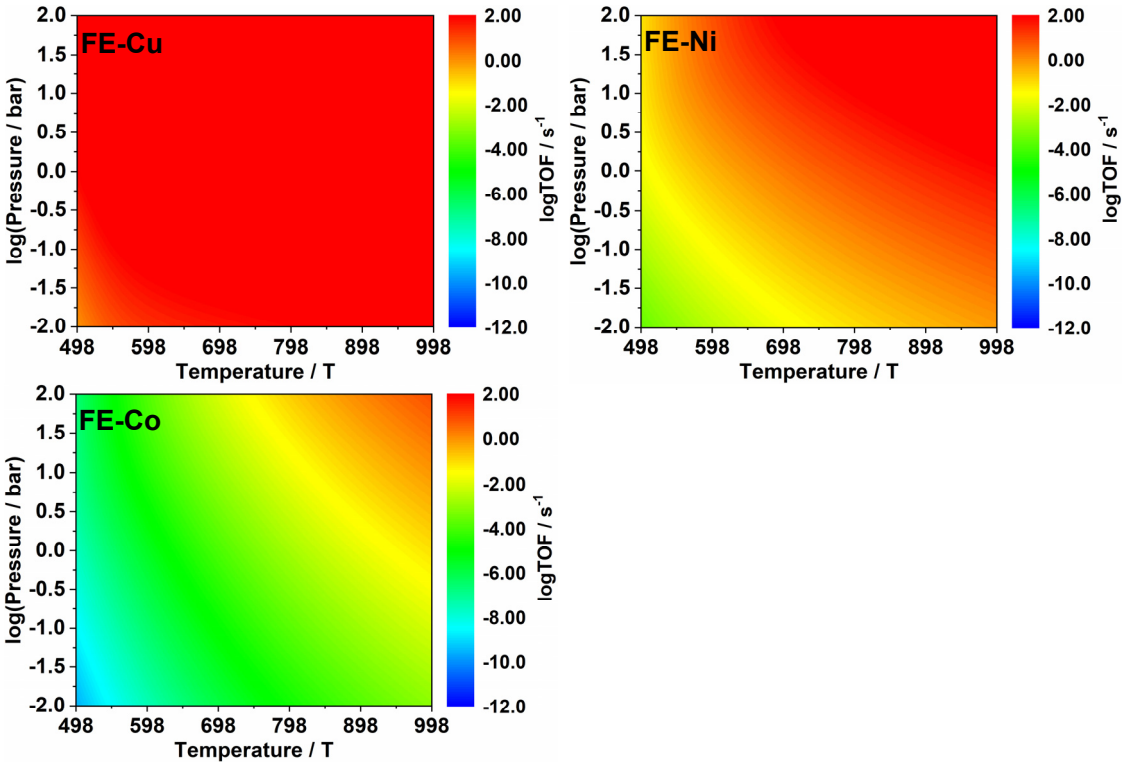

Figure S4. Activity plots of PDH on three kinds of FE-M^{2+} sites as a function of temperature and pressure.