Supporting Information

Insight into the mechanism of the solvolysis of propylene oxide over titanium silicalite-1: A theoretical study

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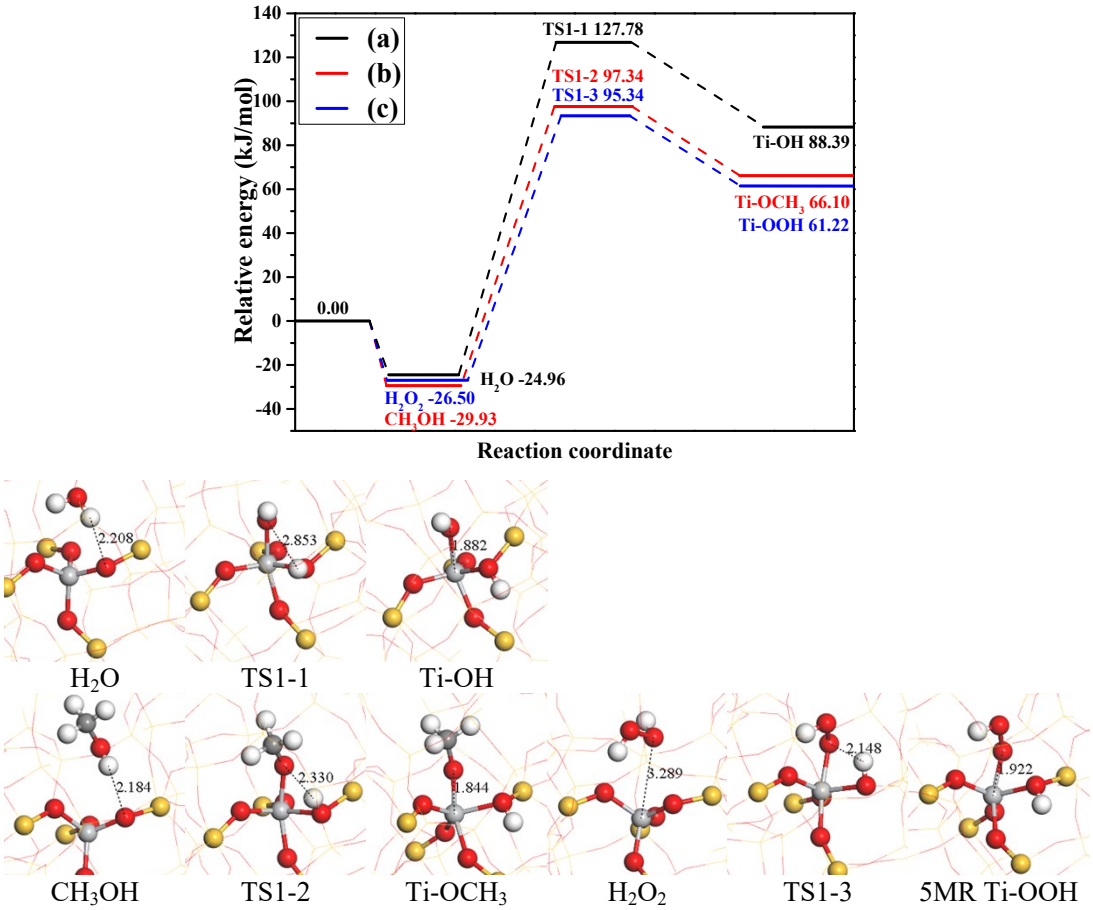

Fig. S1 Potential energy profiles for formations of ring-opening active substances (a) Ti-OH, (b) Ti-CH_3 and (c) 5MR Ti-OOH at 313 K together with together with the structures of reactant, transition state and product at tetrahedral Ti site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

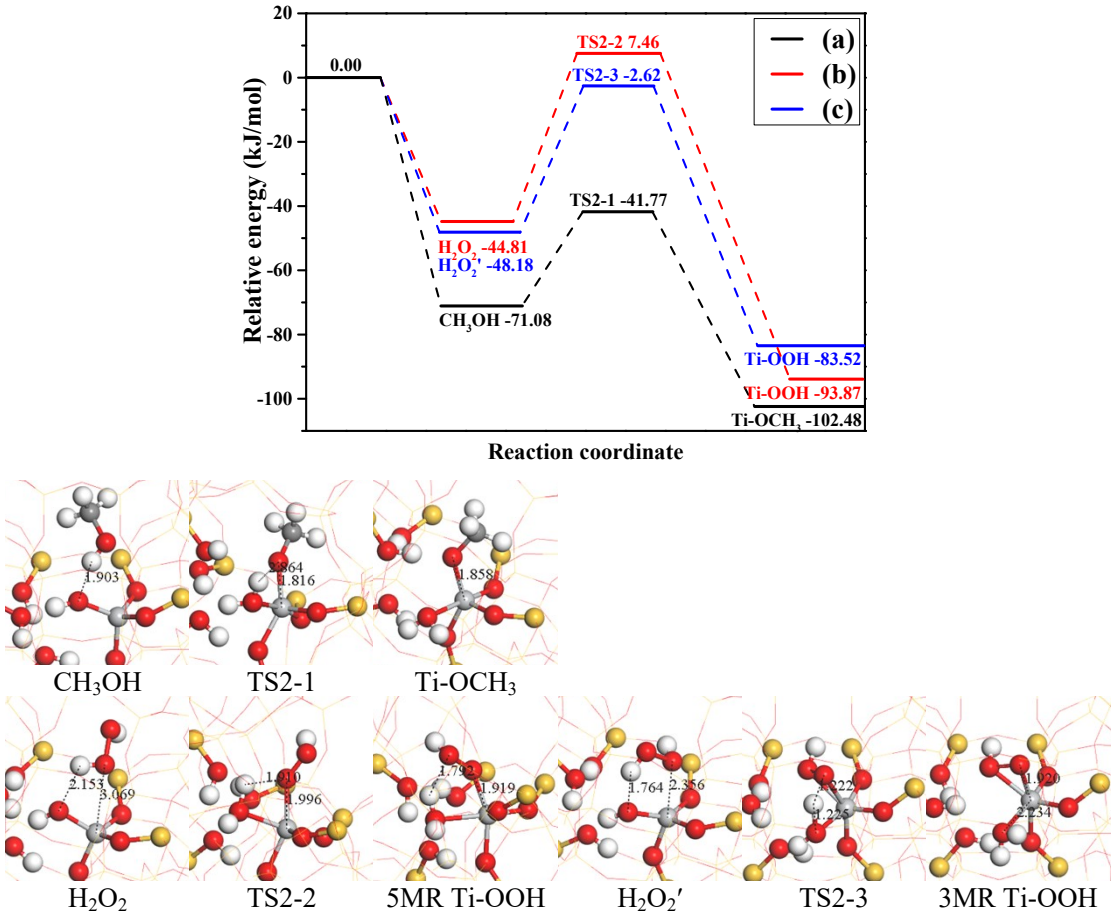

Fig. S2 Potential energy profiles for formation of ring-opening active substances (a) Ti-OCH_3, (b) 5MR Ti-OOH and (c) 3MR Ti-OOH at 313 K together with together with the structures of reactant, transition state and product at Ti/defect site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

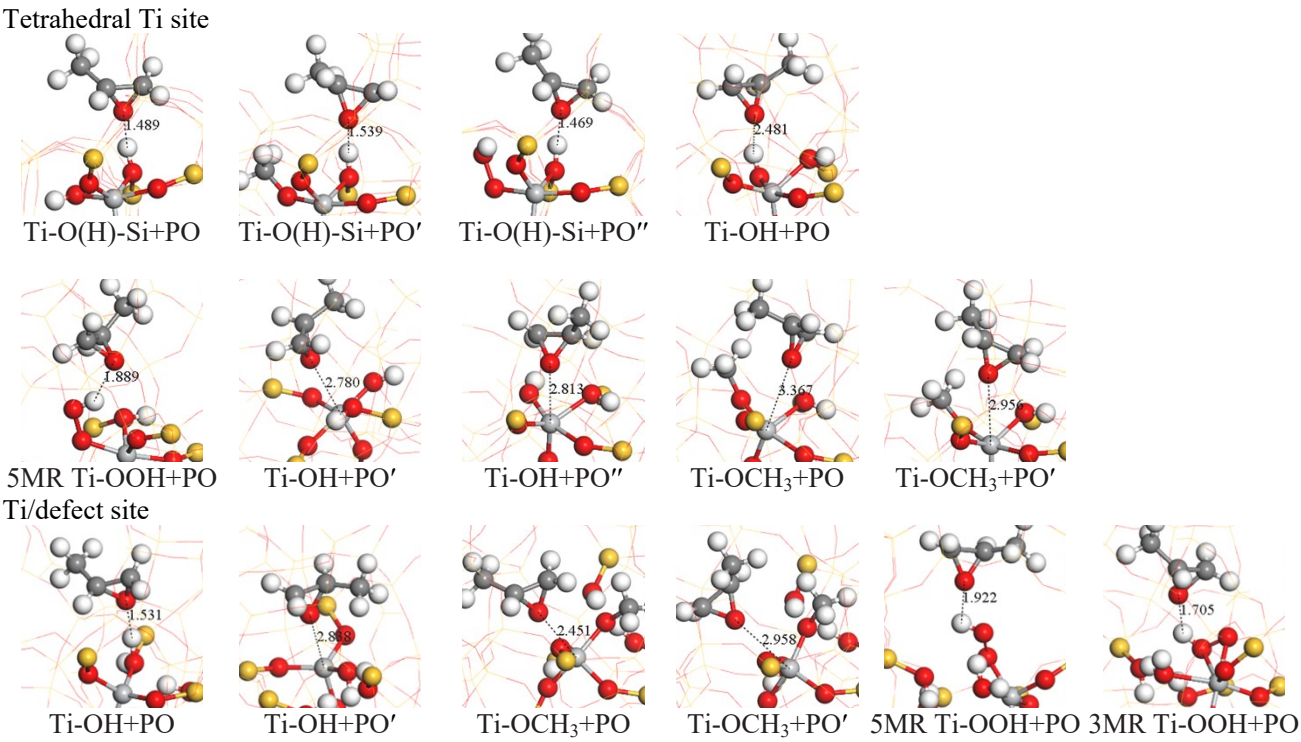

Fig. S3 The stable adsorption configurations of PO over Ti-O(H)-Si, Ti-OH, Ti-OCH_3, 5MR Ti-OOH and 3MR Ti-OOH together with the corresponding adsorption free energies at 313 K. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

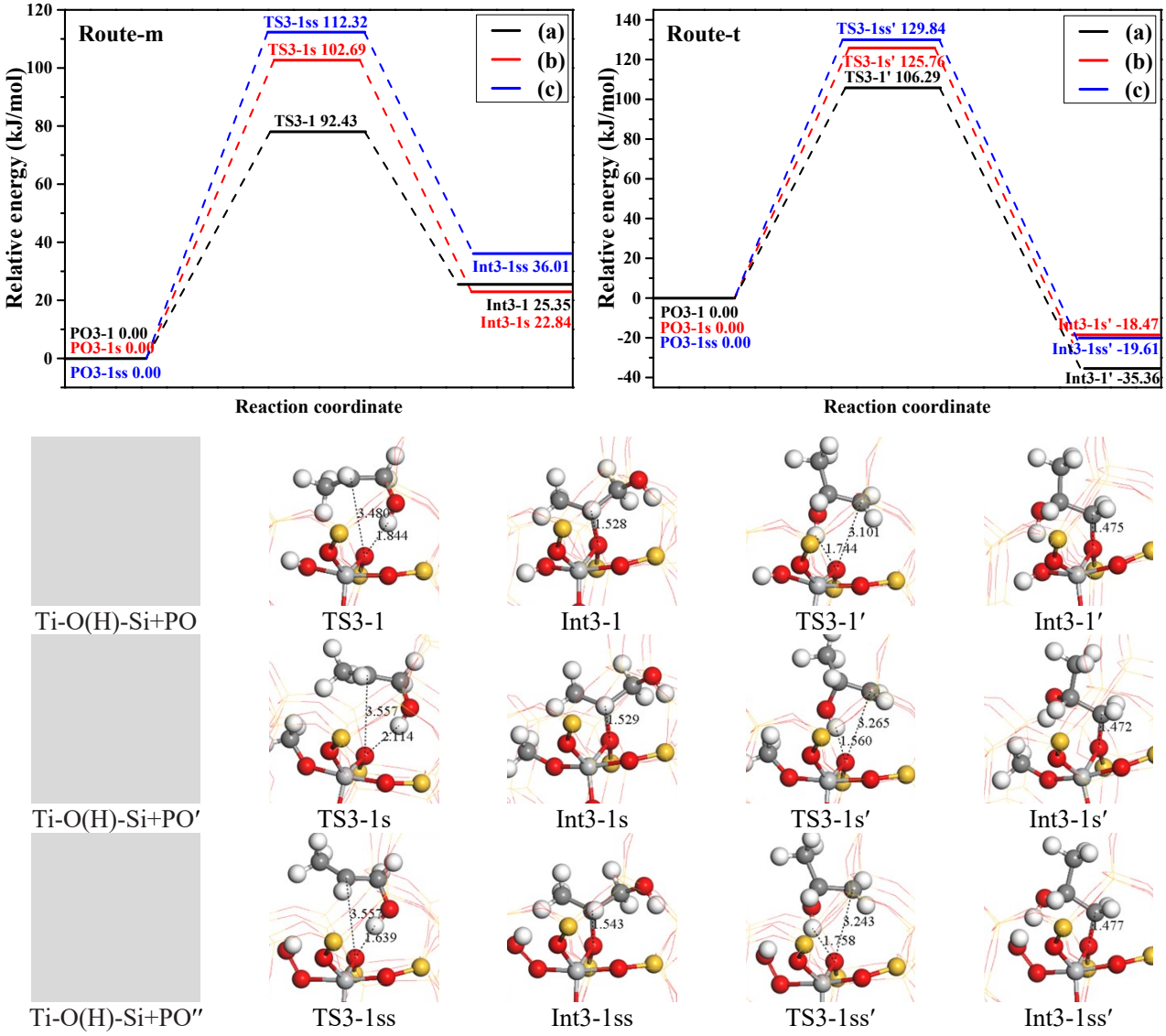

Fig. S4 Potential energy profiles for the Brønsted acid reactions mode of ring-opening of PO with Ti-O(H)-Si adjacent to (a) -OH, (b) -OCH_3 and (c) -OOH groups at 313 K together with together with the structures of reactant, transition state and product at tetrahedral Ti site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

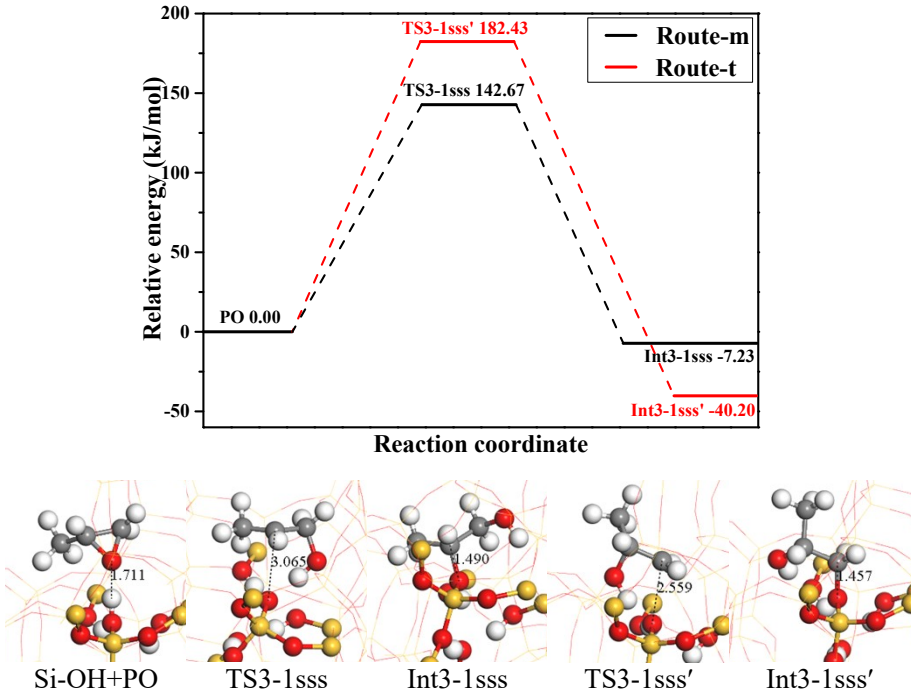

Fig. S5 Potential energy profiles for the Brønsted acid reactions mode of ring-opening of PO with Si-OH at 313 K together with together with the structures of reactant, transition state and product. The energy unit is in kJ/mol, and bond length is in Å. (C = grey, O = red, Si = yellow, H = white).

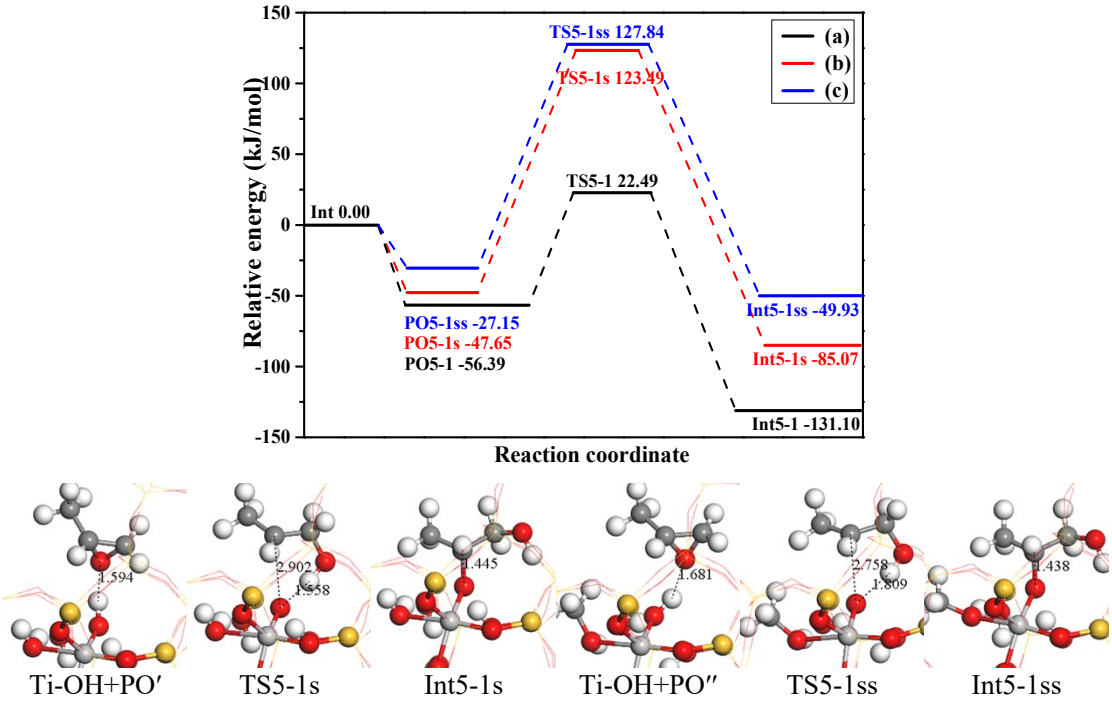

Fig. S6 Potential energy profiles for the Brønsted acid reactions mode of ring-opening of PO with Ti-OH when co-adsorption with a (b) H_2O or (c) CH_3OH at 313 K together with together with the structures of reactant, transition state and product at Ti/defect site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

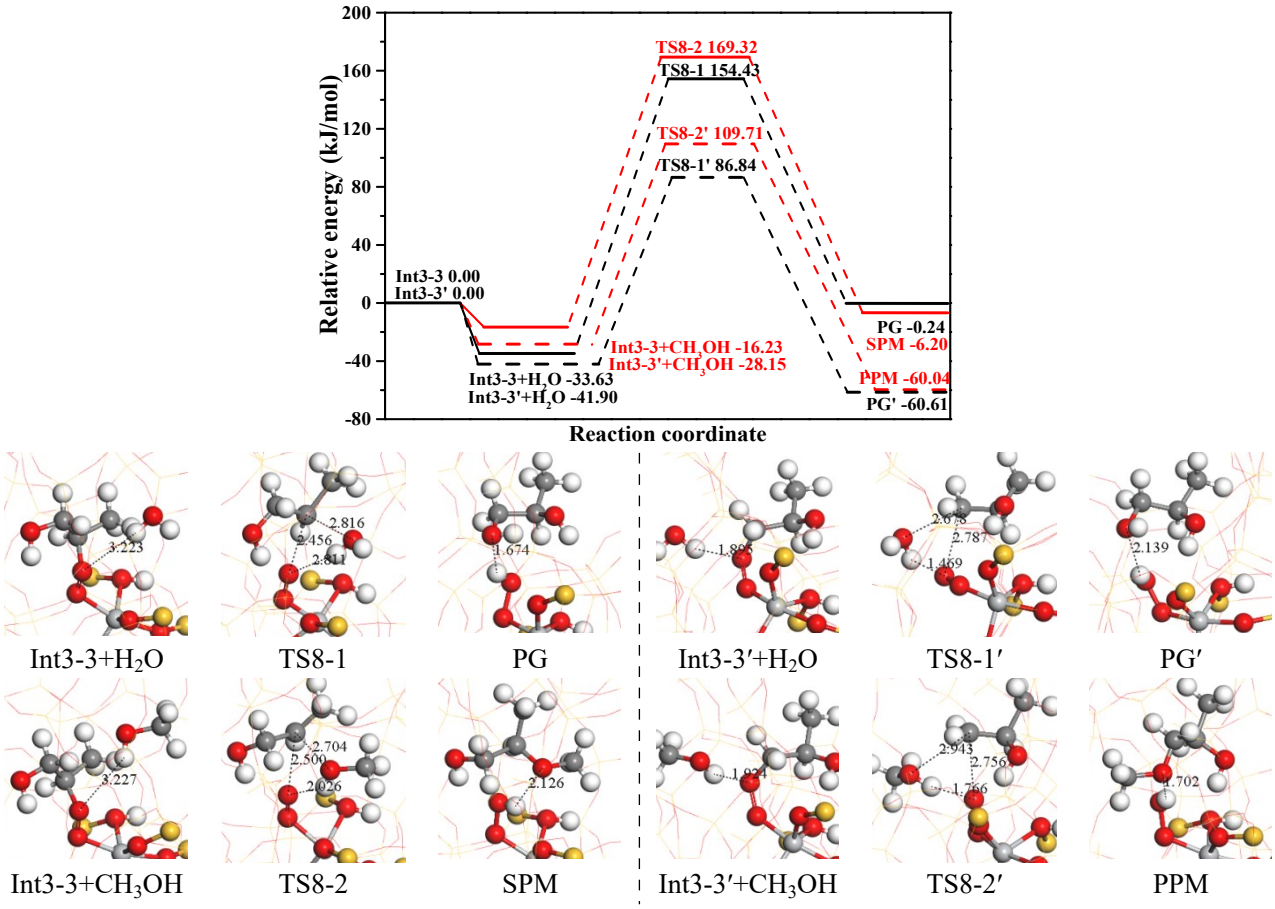

Fig. S7 Potential energy profiles of PG, SPM and PPM formation via 5MR Ti-OOH at 313 K, together with together with the structures of reactant, transition state and product at tetrahedral Ti site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

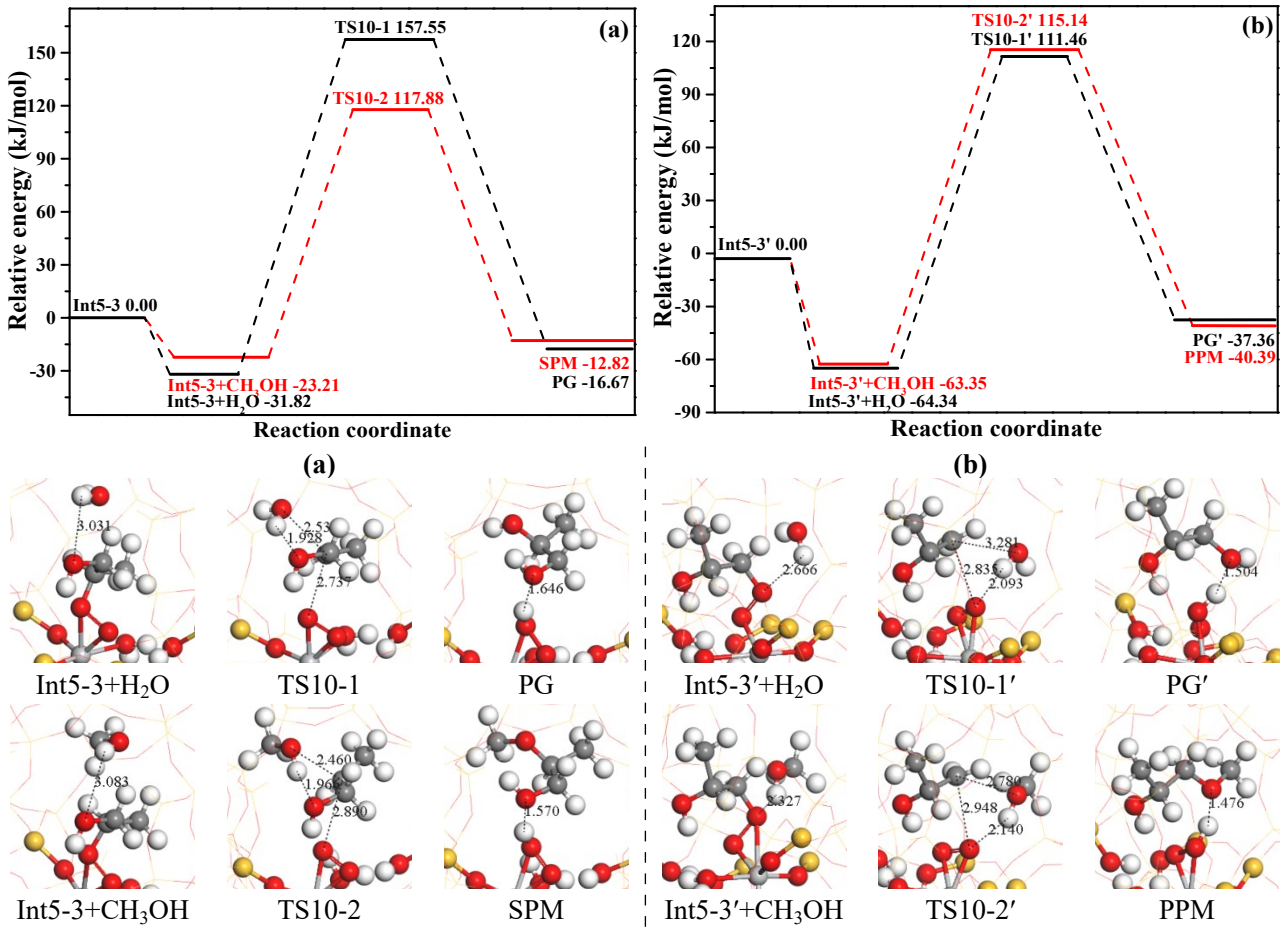

Fig. S8 Potential energy profiles of PG and MME formation via 3MR Ti-OOH at 313 K together with together with the structures of reactant, transition state and product at Ti/defect site. The energy unit is in kJ/mol, and bond length is in Å (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

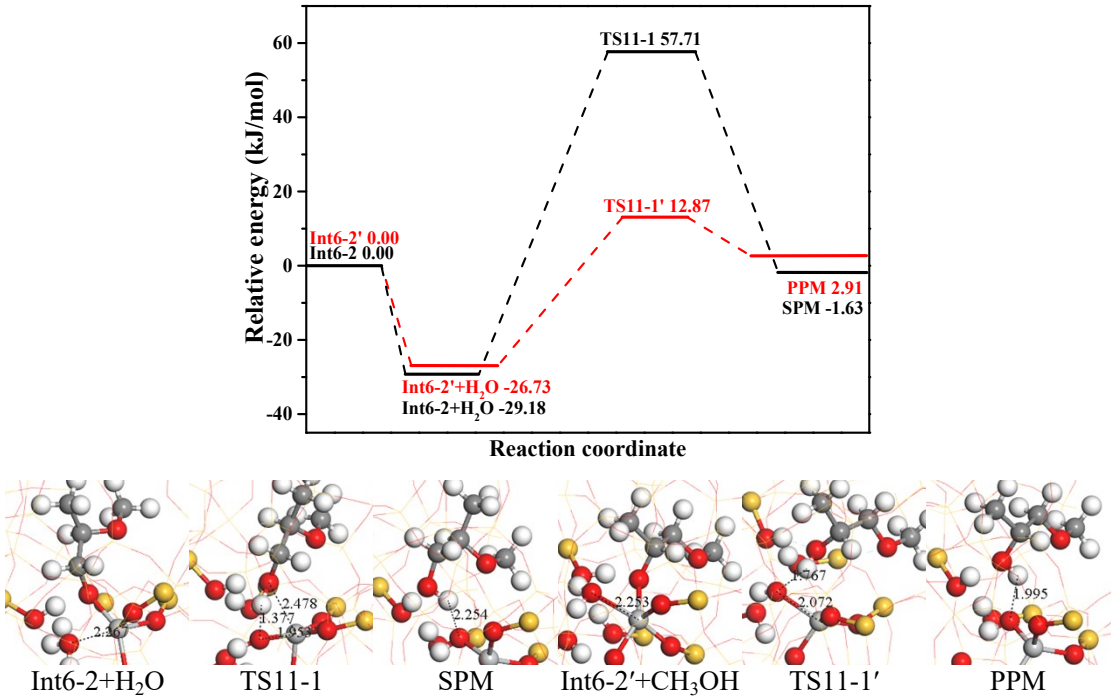

Fig. S9 Potential energy profiles for MME formation *via* hydrolysis of Int6-2 and Int6-2′ at 313 K together with together with the structures of reactant, transition state and product at Ti/defect site. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

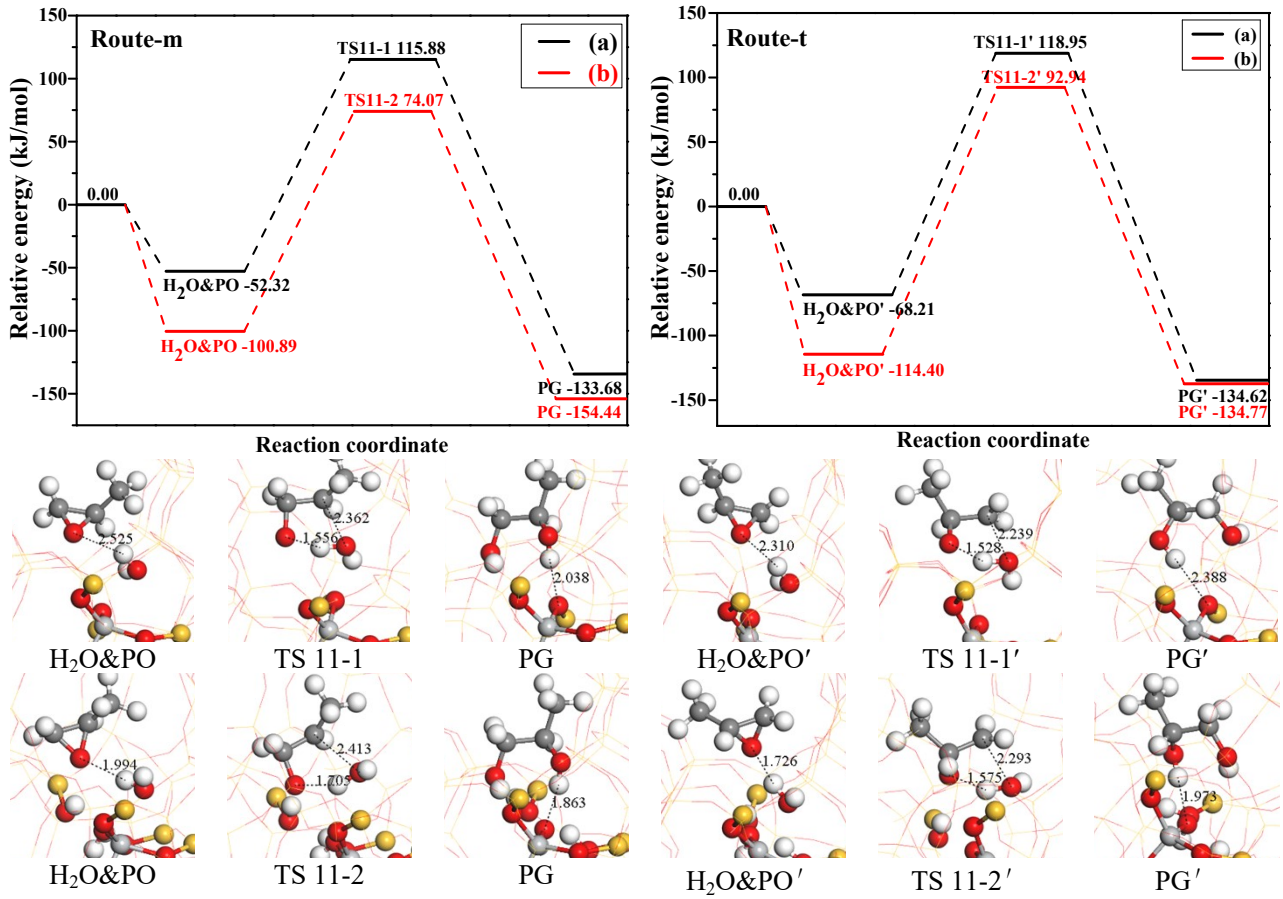

Fig. S10 Potential energy profiles for PG formation *via* concerted mechanism at 313 K together with together with the structures of reactant, transition state and product at (a) tetrahedral Ti and (b) Ti/defect sites. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

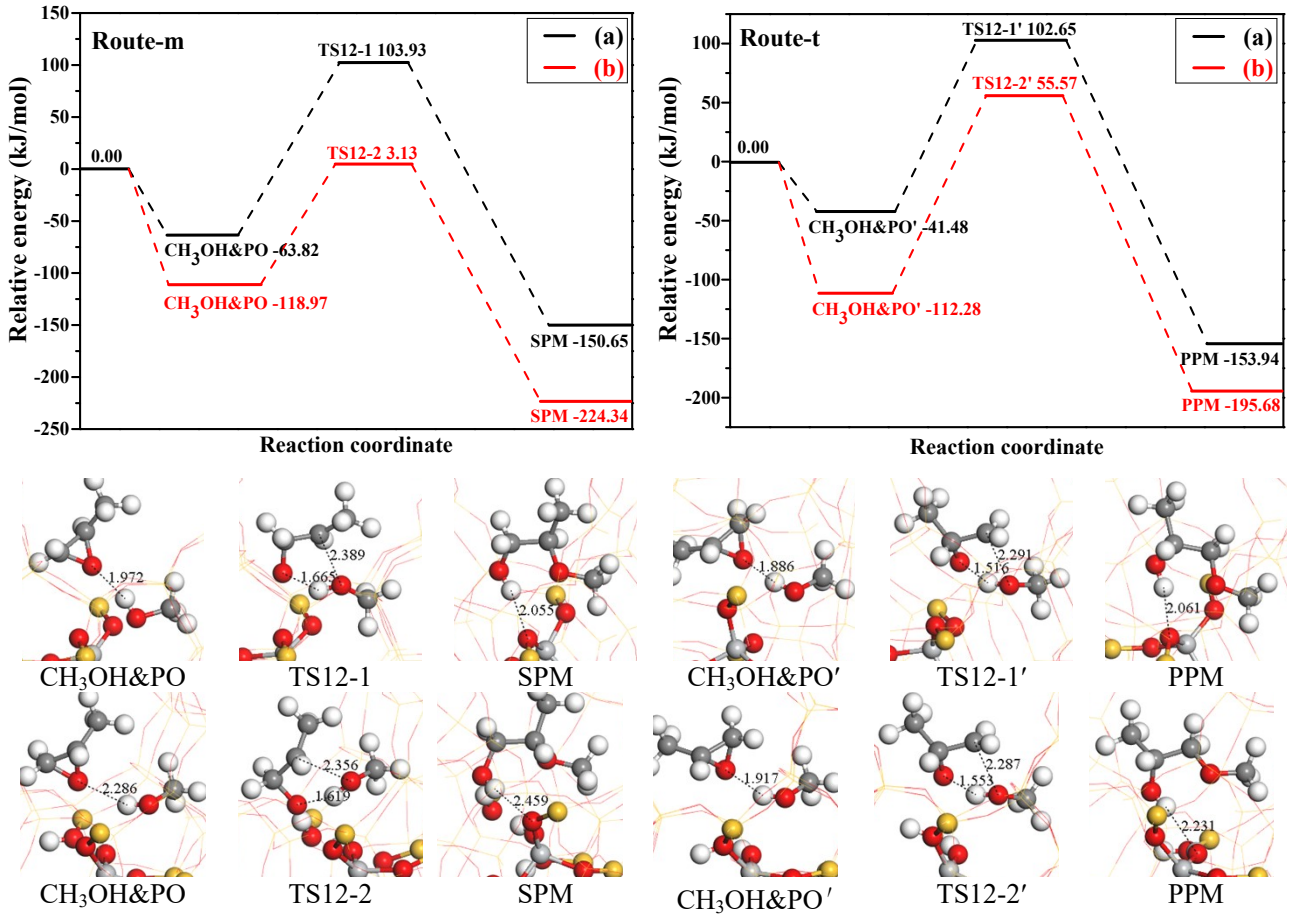

Fig. S11 Potential energy profiles for SPM and PPM formations *via* concerted mechanism at 313 K together with together with the structures of reactant, transition state and product at (a) tetrahedral Ti and (b) Ti/defect sites. The energy unit is in kJ/mol, and bond length is in Å. (Ti = light grey, C = grey, O = red, Si = yellow, H = white).

Table S1 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) of ring-opening active substances formation at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS1-1	152.74	113.35	-316.51
	TS1-2	127.26	96.03	-1058.56
	TS1-3	121.84	87.72	-1034.42
Ti/ddefect site	TS2-1	29.31	-31.40	-630.65
	TS2-1	45.56	-35.34	-658.59
	TS2-3	59.04	-49.06	-793.13

Table S2 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) for Brønsted acid reaction mode of PO with Ti-OH at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral Ti site	TS3-1	92.43	25.35	-262.35
	TS3-1′	106.27	-35.36	-450.01
	TS3-2	102.31	-43.81	-354.92
	TS3-2′	125.66	-67.65	-452.37
Ti/defect site	TS5-1	78.88	-74.71	-444.37
	TS5-1′	136.44	-72.77	-498.61

Table S3 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) for Lewis acid reaction mode of PO with Ti-OH over tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS4-1	167.80	-29.99	-342.06
	TS4-1′	160.68	-21.71	-508.35
Ti/ddefect site	TS6-1	106.51	-89.74	-234.90
	TS6-1′	124.20	-73.49	-499.54

Table S4 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) for Lewis acid reaction mode of PO with Ti-OCH_3 at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS5-1	263.18	-41.22	-303.27
	TS5-1′	289.62	-41.90	-318.17
Ti/ddefect site	TS6-2	89.41	-88.19	-286.60
	TS6-2′	132.11	-95.69	-329.57

Table S5 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm^{-1}) for PO with Ti-OOH at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS3-3	134.25	-17.50	-352.27
	TS3-3′	153.70	-24.23	-368.42
Ti/ddefect site	TS5-2	120.55	-76.51	-378.37
	TS5-2′	217.83	-40.41	-481.83
	TS5-3	52.52	-123.66	-281.55
	TS5-3′	90.80	-96.23	-326.91

Table S6 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm^{-1}) for PG formation via stepwise mechanism at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS7-1	21.36	-93.55	-309.33
	TS7-1′	30.46	-49.56	-325.64
	TS8-1	188.06	33.38	-332.83
	TS8-1′	128.75	-18.70	-280.02
Ti/defect site	TS9-1	50.19	28.46	-151.31
	TS9-1′	73.29	65.45	-218.87
	TS9-2	72.24	43.86	-253.81
	TS9-2′	42.18	8.47	-214.09
	TS10-1	189.37	15.15	-269.82
	TS10-1′	175.80	26.98	-234.44

Table S7 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm^{-1}) for MME formation via stepwise mechanism at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS7-2	11.67	-99.10	-281.14
	TS7-2′	34.93	-32.95	-345.37
	TS8-2	185.55	10.04	-364.02
	TS8-2′	137.86	-31.89	-345.37
Ti/ddefect site	TS9-3	188.24	-8.99	-337.34
	TS9-3′	146.29	-17.15	-290.49
	TS10-2	141.09	10.39	-294.66
	TS10-2′	178.49	22.96	-327.77
	TS11-1	86.89	27.56	-302.84
	TS11-1′	39.60	29.64	-300.94

Table S8 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) of MME formation *via* concerted mechanism at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS11-1	168.20	-81.36	-464.38
	TS11-1′	187.16	-66.41	-556.30
Ti/ddefect site	TS11-2	174.96	-53.55	-412.72
	TS11-2′	207.34	-83.40	-448.98

Table S9 The corresponding activation free energy (G_a, kJ/mol), reaction free energies (ΔG, kJ/mol) and the only one imaginary frequency of transition states (v, cm-1) of MME formation *via* concerted mechanism at tetrahedral Ti and Ti/defect sites (T=313 K).

TS-1 models	TSs	G_a, kJ/mol	ΔG, kJ/mol	v, cm^{-1}
Tetrahedral site	TS12-1	167.75	-86.83	-544.34
	TS12-1′	144.13	-112.46	-517.88
Ti/ddefect site	TS12-2	122.10	-105.37	-562.16
	TS12-1′	167.85	-83.40	-534.01