Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

DFT Investigations for the Reaction Mechanism of Dimethyl Carbonate Synthesis on Pd(II)/β Zeolites

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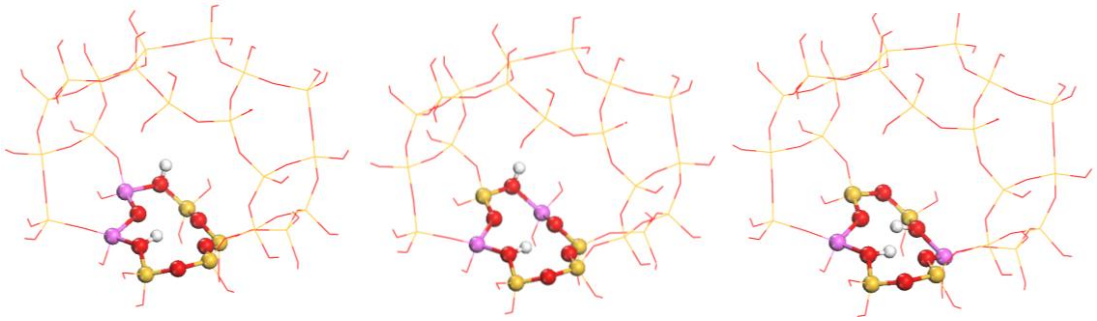
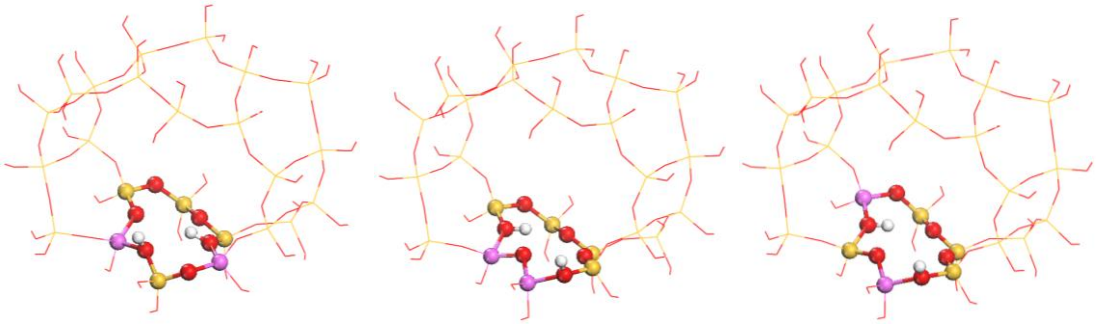
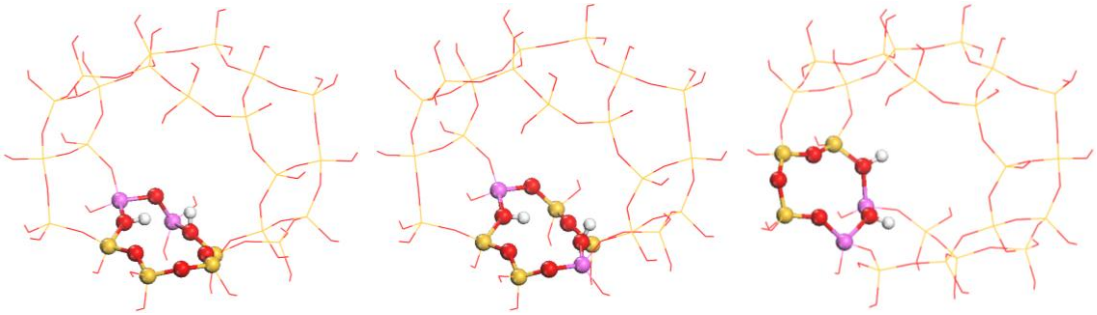
Supporting Figures



A B C



D E F



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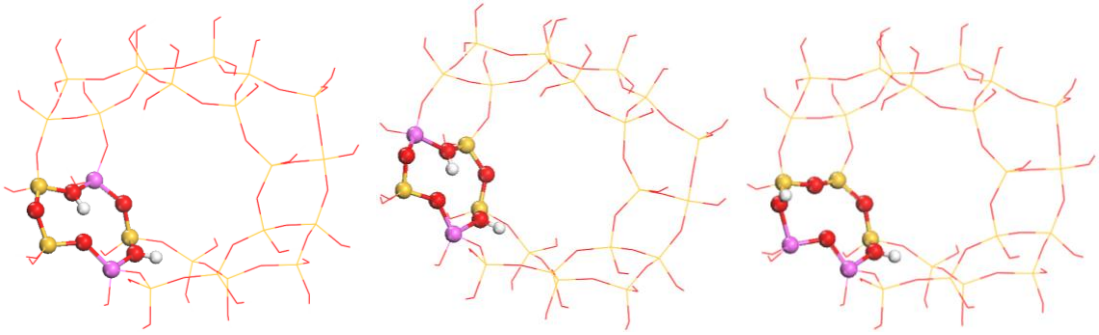

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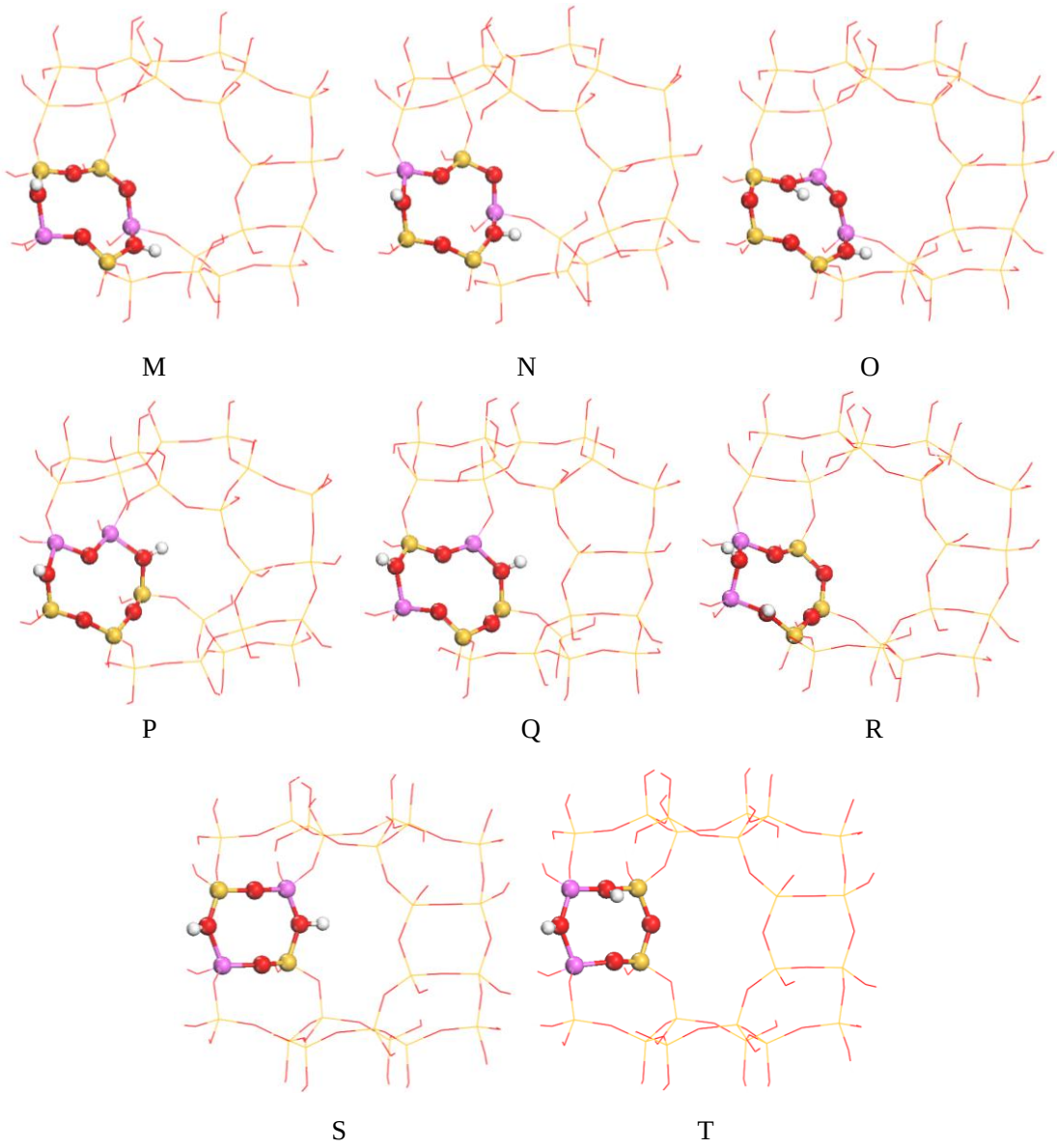


Figure S1. Different Aluminum-distribution structures for the β-zeolite (Two hydrogen atoms are added to compensate the negative charges caused by the replacement of slicon atoms to aluminum atoms.).

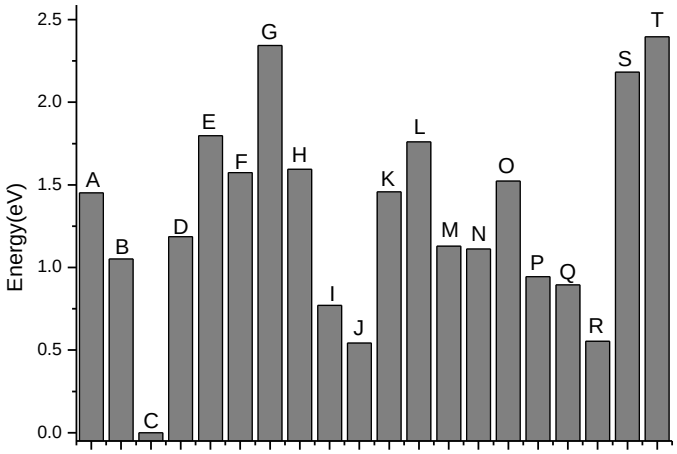


Figure S2. Energy differences among the different Aluminum-distribution of the β-zeolite. Zero of the energy scale corresponds to the Structure C in Fig. S1. Obviously, Structure C, J and S are most stable Aluminum-distribution forms for six, five and four member ring. So, in Fig. S3 we choose these three structures to represent the inequivalent positions for the location of Pd^{2+} cation.

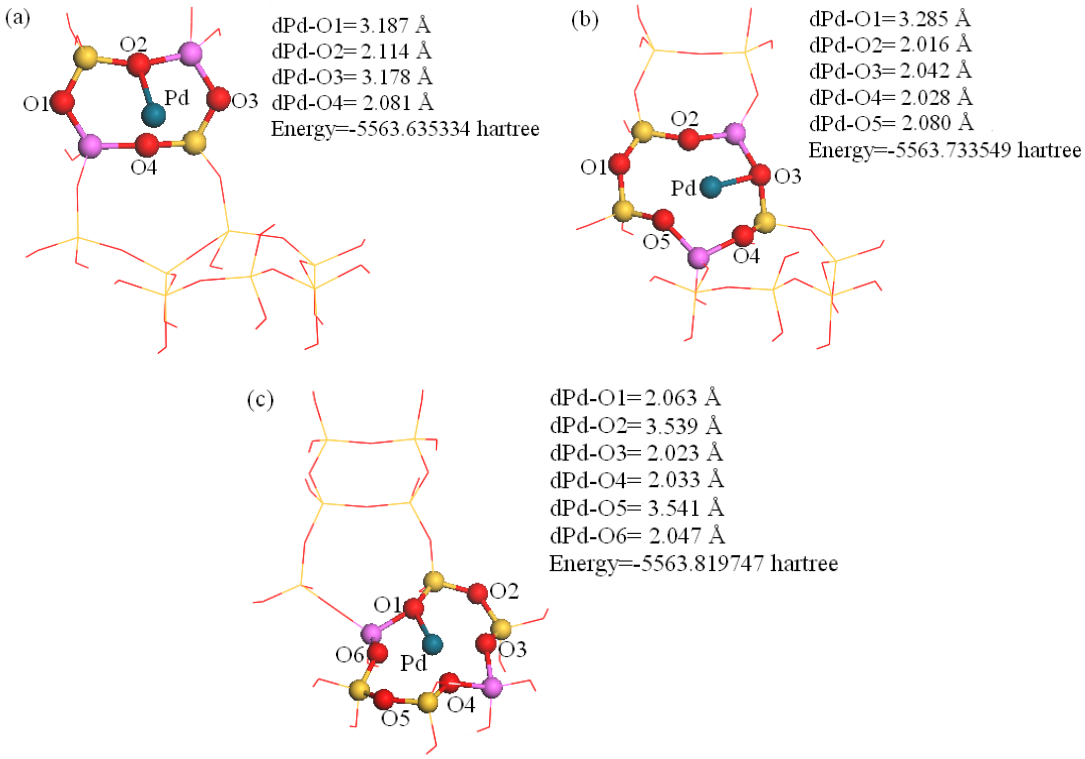


Figure S3. Optimization structure and energy for all the possible Pd(II) sites on β zeolite. (a: Pd(II) cation on four-member ring, b: Pd(II) cation on five-member ring, C: Pd(II) cation on six-member ring).

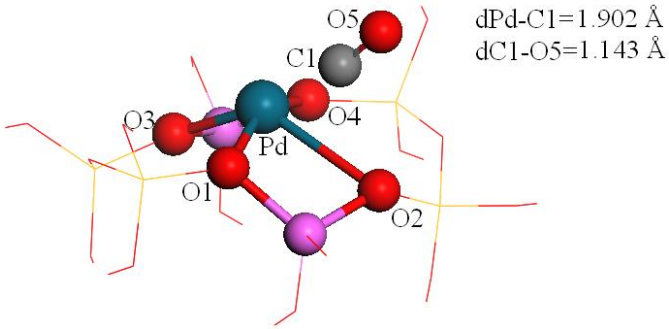


Figure S4. Optimization structure for the CO-Pd(II)/β.

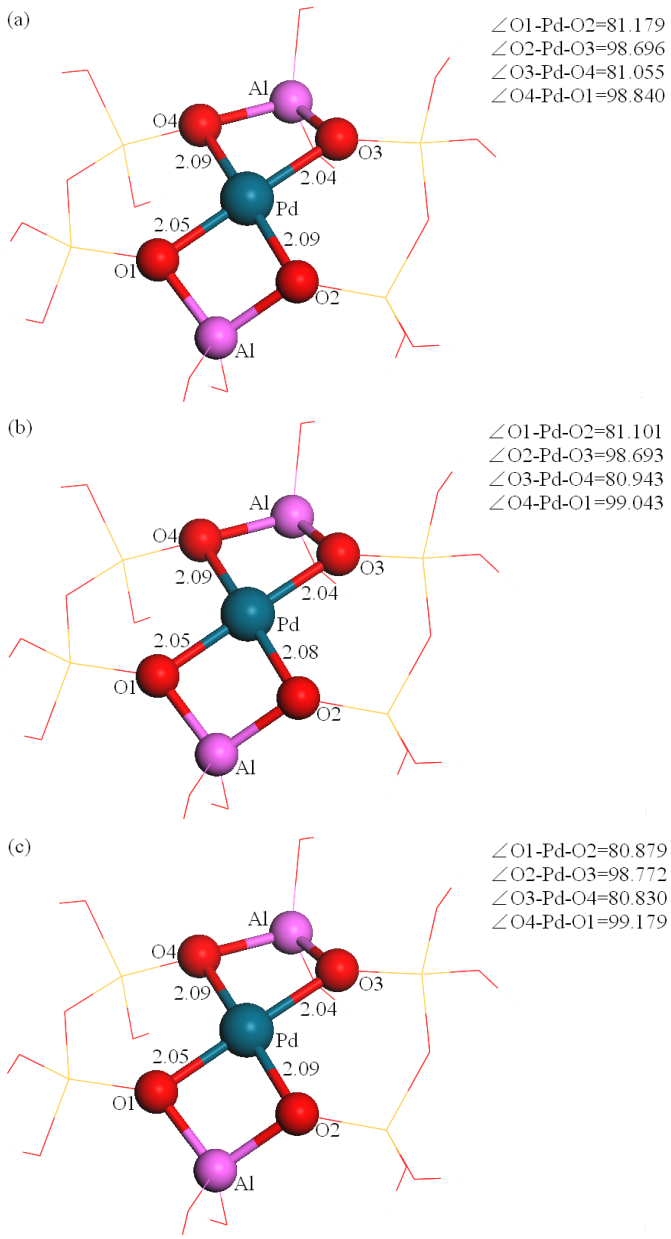
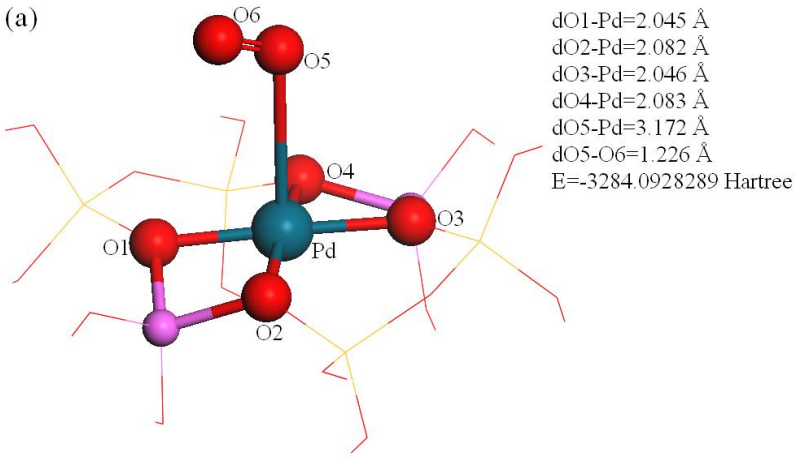


Figure S5. Optimized structure for the Pd(II)/β catalyst under different convergence criteria (a: Medium/DNP, b:Fine/DNP, C: Fine/DNP(all-electron relativistic)).



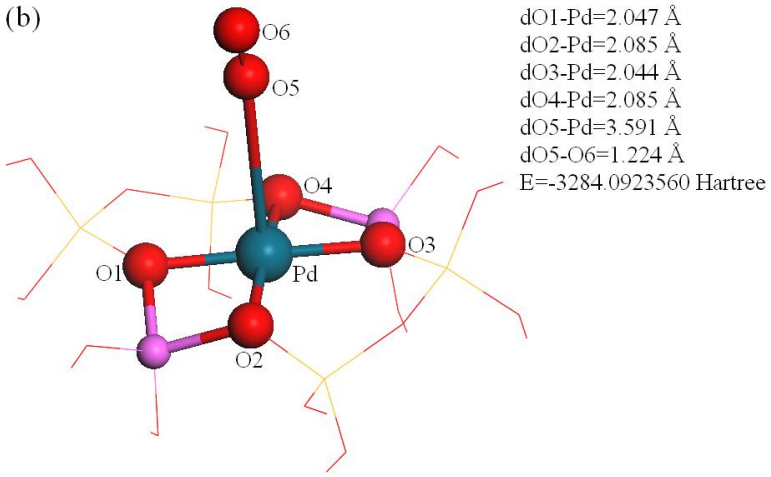


Figure S6. Optimized structure for O_2 adsorption (a: ground state(spin multiplicity=3), b: excited state(spin multiplicity=1)).

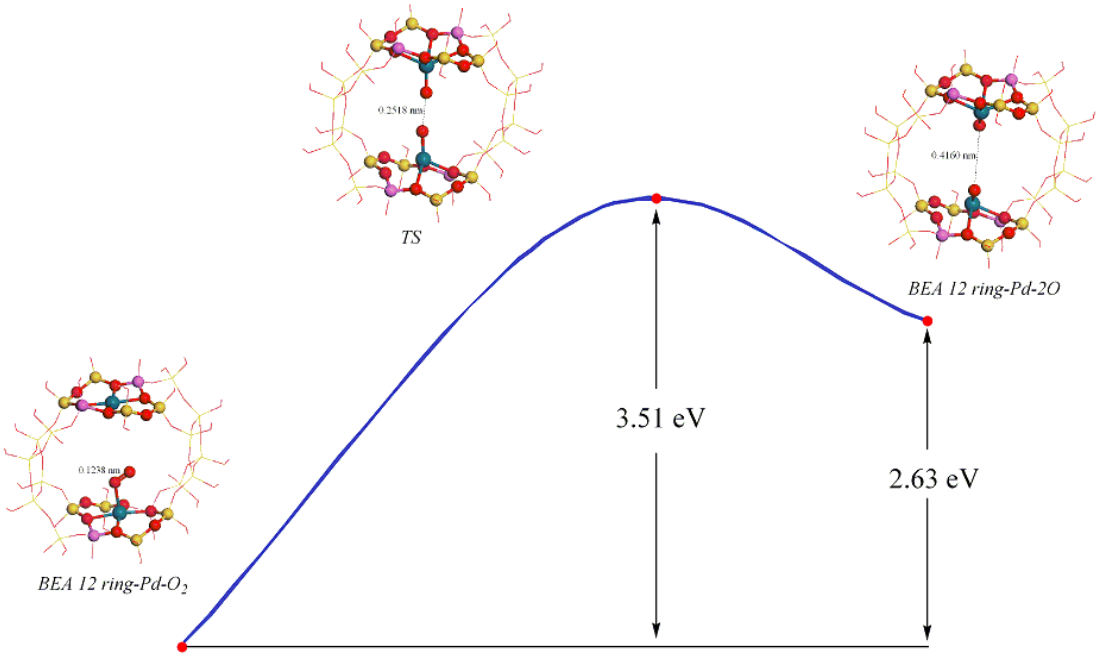
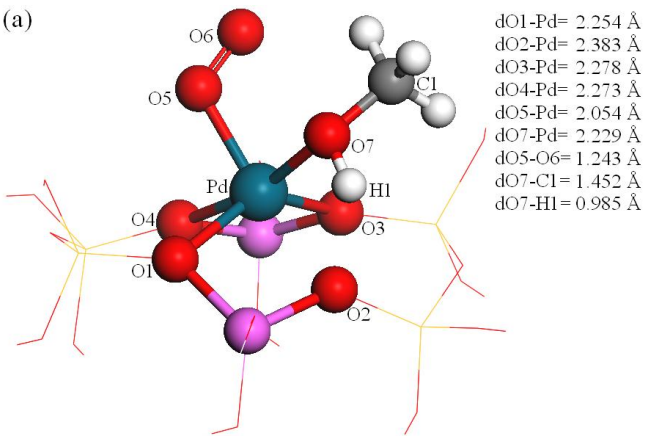


Figure S7. Reaction coordinate for O_2 decomposition on Pd(II)/β.



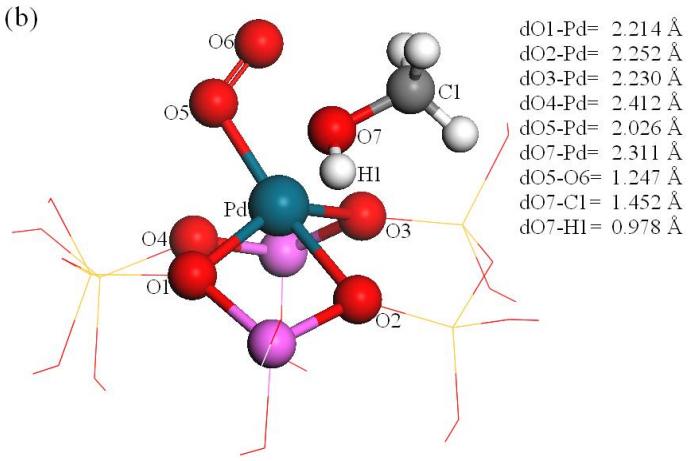


Figure S8. Optimized structure for the coadsorption of O_2 and methanol (a: ground state(spin multiplicity=3), b: excited state(spin multiplicity=1)).

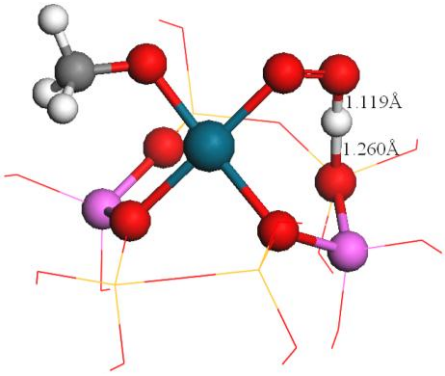


Figure S9. Optimized structure for the $(CH_3O)(OOH)$–Pd(II)/β.

Supporting Tables:

Table S1. Structural parameters and WBIs of the reactant complex, transition state and product complex of CO insertion reaction (PathI) [Bond length/Å].

	CH_3O–OH–CO		TS		CH_3OCOOH	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.669	0.073	2.540	0.116	2.068	0.297
Pd-O2	2.165	0.196	2.150	0.237	2.103	0.293
Pd-O3	3.073	0.026	2.922	0.049	2.102	0.299
Pd-O4	2.124	0.221	2.176	0.136	2.068	0.301
Pd-O5	1.989	0.620	2.084	0.509	3.098	0.015
Pd-O6	2.107	0.592	2.189	0.466	3.433	0.008
Pd-C1	1.932	0.554	1.898	0.554	3.857	0.002
C1-O7	1.136	2.346	1.157	2.178	1.216	1.681
C1-O5	2.611	0.095	2.023	0.321	1.350	1.013
C1-O6	2.814	0.070	1.998	0.354	1.345	1.020
C2-O6	1.389	1.016	1.422	0.949	1.448	0.861
O5-H	0.988	0.695	0.976	0.707	0.979	0.678

Table S2. Structural parameters and WBIs of the reactant complex, transition state and product complex of DMC formation reaction (PathI) [Bond length/Å].

	MMC–CH_3OH		TS		DMC–H_2O	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.973	0.011	3.032	0.012	2.398	0.114
Pd-O2	2.118	0.292	2.113	0.272	2.089	0.343
Pd-O3	3.132	0.012	2.143	0.008	3.046	0.013
Pd-O4	2.073	0.302	3.403	0.217	2.238	0.219
Pd-O5	3.124	0.007	2.939	0.008	2.117	0.353
Pd-O6	2.211	0.192	2.315	0.104	2.777	0.030
Pd-O7	2.091	0.355	2.011	0.572	2.609	0.063
C1-O5	1.333	1.065	1.491	0.722	3.906	0.001
C1-O6	1.393	0.877	1.329	1.036	1.348	1.011
C1-O7	3.492	0.001	2.785	0.013	1.348	0.971
C2-O7	1.455	0.867	1.428	0.914	1.462	0.843
C1-O8	1.204	1.749	1.179	1.893	1.211	1.693
C3-O6	1.474	0.811	1.500	0.776	1.454	0.827
O5-H1	0.977	0.682	0.987	0.604	1.026	0.578
O7-H2	1.011	0.592	1.682	0.135	3.194	N/A
O5-H2	2.789	0.001	1.077	0.604	0.975	0.714

Table S3. Structural parameters and WBIs of the reactant complex, transition state and product complex of di-methoxide formation reaction (PathII) [Bond length/nm]

	CH_3O–OH–CH_3OH		TS		$(CH_3O)_2$–H_2O	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.297	0.141	2.326	0.137	2.408	0.114
Pd-O2	2.159	0.194	2.119	0.248	2.207	0.241
Pd-O3	3.110	0.017	3.131	0.013	3.196	0.010
Pd-O4	2.344	0.230	2.303	0.203	2.277	0.157
Pd-O5	1.972	0.643	2.045	0.454	2.202	0.272
Pd-O6	1.996	0.632	2.001	0.618	1.994	0.653
Pd-O7	2.249	0.270	2.137	0.435	1.982	0.653
C1-O6	1.397	0.985	1.400	0.984	1.396	0.989
C2-O7	1.442	0.873	1.421	0.906	1.402	0.972
O5-H1	0.988	0.682	1.008	0.623	1.022	0.574
O7-H2	0.985	0.659	1.255	0.339	2.518	0.003
O5-H2	2.121	0.022	1.260	0.345	0.977	0.704

Table S4. Structural parameters and WBIs of the reactant, transition state and product of CO insertion reaction from (PathII) [Bond length/nm].

	double-CH_3O-CO		TS		DMC	
	Bond length	WBI	Bond length	WBI	Bond length	WBI

Pd-O1	2.838	0.053	2.108	0.296	2.068	0.303
Pd-O2	2.198	0.176	2.154	0.276	2.125	0.284
Pd-O3	3.126	0.032	2.150	0.265	2.120	0.288
Pd-O4	2.131	0.221	2.064	0.318	2.069	0.304
Pd-O5	1.997	0.609	3.206	0.009	3.144	0.014
Pd-O6	2.131	0.542	2.895	0.023	3.074	0.016
Pd-C1	1.956	0.536	3.398	0.004	3.714	0.002
C1-O5	2.636	0.076	1.347	1.035	1.349	1.010
C1-O6	3.016	0.060	1.381	0.925	1.350	1.007
C1-O7	1.139	2.329	1.212	1.730	1.216	1.672
C2-O5	1.401	0.980	1.454	0.848	1.447	0.859
C3-O6	1.390	1.010	1.462	0.848	1.447	0.858

Table S5. Structural parameters and WBIs of the reactant, transition state and product of H_2CO formation reaction [Bond length/nm].

	$CH_2(OH)_2$		TS		H_2CO-H_2O	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.116	0.354	2.089	0.373	2.202	0.260
Pd-O2	2.482	0.153	2.342	0.214	2.154	0.284
Pd-O3	2.555	0.039	2.545	0.027	2.722	0.026
Pd-O4	2.420	0.171	2.421	0.176	3.145	0.014
Pd-O5	2.177	0.309	3.658	0.011	2.101	0.343
Pd-O6	3.362	0.009	2.133	0.247	2.229	0.243
C1-O5	1.465	0.825	1.217	1.880	1.233	1.727
C1-O6	1.384	1.009	2.534	0.025	3.767	0.002
O5-H1	0.996	0.617	3.480	0.001	3.458	N/A
O6-H1	2.595	0.002	0.991	0.593	0.995	0.639
O6-H2	0.978	0.714	0.967	0.692	0.975	0.713

Table S6. Structural parameters and WBIs of the reactant, transition state and product of HCOOH formation reaction [Bond length/nm].

	H_2CO-O		TS		HCOOH	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.557	0.098	2.219	0.237	2.004	0.418
Pd-O2	2.141	0.213	2.665	0.080	2.527	0.118
Pd-O3	2.098	0.276	2.400	0.136	2.678	0.017
Pd-O4	3.031	0.020	2.434	0.125	2.152	0.303
Pd-O5	2.123	0.252	2.509	0.112	3.161	0.028
Pd-O6	1.807	1.206	1.975	0.618	2.183	0.209
C1-O5	1.227	1.762	1.174	2.104	1.197	1.868
C1-O6	2.795	0.014	2.301	0.279	1.386	0.923
C1-H2	1.104	0.907	1.681	0.103	2.016	0.001

O6-H2	2.185	0.019	1.008	0.690	1.014	0.575

Table S7. Structural parameters and WBIs of the reactant, transition state and product of $HCOOCH_3$ formation reaction [Bond length/nm].

	HCOOH-CH_3OH		TS		MF-H_2O	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.914	0.009	2.809	0.025	2.748	0.021
Pd-O2	2.075	0.294	2.052	0.353	2.050	0.331
Pd-O3	2.042	0.310	2.080	0.326	2.062	0.318
Pd-O4	3.119	0.006	3.152	0.010	3.100	0.008
Pd-O5	2.092	0.261	2.090	0.310	2.092	0.321
Pd-O6	2.067	0.351	2.225	0.181	2.172	0.208
C1-O5	1.377	0.935	3.362	0.002	4.435	N/A
C1-O6	3.812	0.001	1.402	0.899	1.401	0.894
O5-H1	1.072	0.492	0.967	0.697	0.978	0.702
O5-H2	3.228	N/A	1.009	0.634	1.039	0.562
O6-H2	1.023	0.576	3.192	N/A	3.712	N/A

Table S8. Structural parameters and WBIs of the reactant, transition state and product of CH_3OCH_2OH formation reaction [Bond length/nm].

	CH_2O -CH_3OH		TS		CH_3OCH_3OH	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.900	0.012	2.690	0..030	2.197	0.226
Pd-O2	2.098	0.274	2.096	0.304	2.047	0.325
Pd-O3	2.037	0.343	2.024	0.380	2.102	0.296
Pd-O4	3.089	0.014	2.952	0.016	2.895	0.009
Pd-O5	2.063	0.365	2.341	0.175	3.357	0.011
Pd-O6	2.079	0.316	2.061	0.327	2.068	0.333
Pd-C1	2.222	0.294	2.506	0.100	3.092	0.016
C1-O5	2.950	0.029	2.374	0.056	1.395	0.925
C1-O6	1.272	1.551	1.245	1.655	1.416	0.881
O5-H1	1.034	0.552	0.982	0.642	2.664	0.001
O6-H1	3.384	N/A	3.147	0.001	1.037	0.537

Table S9. Structural parameters and WBIs of the reactant, transition state and product of DMM formation reaction [Bond length/nm].

	CH_3OCH_2OH -CH_3OH		TS		DMM-H_2O	
	Bond length	WBI	Bond length	WBI	Bond length	WBI
Pd-O1	2.220	0.200	2.823	0.041	2.820	0.021
Pd-O2	2.043	0.304	2.493	0.060	2.058	0.322
Pd-O3	2.205	0.177	2.126	0.216	2.064	0.299

Pd-O4	2.963	0.011	3.058	0.020	3.106	0.009
Pd-O5	2.646	0.059	1.968	0.690	2.088	0.320
Pd-O6	2.035	0.405	2.107	0.296	2.156	0.238
C1-O5	1.417	0.911	3.374	0.004	4.236	0.007
C1-O6	4.567	N/A	1.528	0.764	1.428	0.849
O5-H1	0.973	0.711	0.973	0.738	0.980	0.702
O5-H2	4.235	N/A	3.327	0.012	1.031	0.577
O6-H2	1.039	0.544	3.378	0.003	3.759	N/A