catalysts

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Supplementary Information

A Mechanistic Study of Methanol Steam Reforming on Ni_2P Catalyst

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Section S1. Details of density functional calculations of thermochemical properties

Frequency calculations were performed on gas phase molecules and all optimized adsorbed species to determine zero-point vibrational energies (ZPVE), and vibrational, translational and rotational enthalpy and free energy. These terms were then used, together with electronic energies (E_0, provided by VASP), to estimate enthalpies (H)

$$H = E_0 + \mathrm{ZPVE} + H_{\mathrm{vib}} + H_{\mathrm{trans}} + H_{\mathrm{rot}} \quad \text{(S1)}$$

and free energies (G)

$$G = E_0 + \mathrm{ZPVE} + G_{\mathrm{vib}} + G_{\mathrm{trans}} + G_{\mathrm{rot}} \quad \text{(S2)}$$

for reactants, products, and transition states at 593 K (the temperature at which ethane hydrogenolysis rates were measured). For calculations which include a periodic metal surface or a metal half-particle, there are no translational or rotational degrees of freedom and DFT-derived vibrational frequencies can be used to determine the ZPVE, H_{vib}, and G_{vib}

$$ZPVE = \sum_i (\tfrac{1}{2} \nu_i h) \quad \text{(S3)}$$

$$H_{vib} = \sum_i \left(\frac{\nu_i h e^{\frac{-\nu_i h}{kT}}}{1 - e^{\frac{-\nu_i h}{kT}}} \right) \quad \text{(S4)}$$

$$G_{vib} = \sum_i \left(-kT \ln \frac{1}{1 - e^{\frac{-\nu_i h}{kT}}} \right) \quad \text{(S5)}$$

For gaseous molecules, translational and rotational enthalpies and free energies were also computed from statistical mechanics:

$$H_{trans} = \frac{5}{2} kT \quad \text{(S6)}$$

$$H_{rot,linear} = kT \quad \text{(S7)}$$

$$H_{rot,nonlinear} = \frac{3}{2} kT \quad \text{(S8)}$$

$$G_{trans} = -kT \ln \left[\left(\frac{2\pi MkT}{h^2} \right)^{3/2} V \right] \quad \text{(S9)}$$

$$G_{rot} = -kT \ln \left[\frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\theta_x \theta_y \theta_z} \right)^{1/2} \right] \quad \text{(S10)}$$

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \quad \text{(S11)}$$

where I_i is the moment of inertia about axes x, y or z and σ is the symmetry number of the molecule (2 for H_2 and 6 for C_2H_6). Equations S10–S12 obtained from: McQuarrie, D. A.; Statistical Mechanics; Sausolito, CA.

Table S1: Electronic energy, ZPVE, and vibrational, translational, and rotational enthalpy and free energy at 573 K in eV.

Systems	**E0**	**ZPVE**	**H(v)**	**G(v)**	**H(t+r)**	**G(t+r)**
$Ni_2P(001)$	-374.7250	-	-	-	-	-
Molecules	**E0**	**ZPVE**	**H(v)**	**G(v)**	**H(t+r)**	**G(t+r)**
H_2	-6.9767	0.2695	0.0000	0.0000	0.1728	-0.7147
CH_3OH	-29.8848	1.3426	0.0967	-0.1138	0.1975	-1.3091
H_2O	-14.1521	0.5651	0.0038	-0.0009	0.1975	-1.0545
CH_2O	-21.8274	0.6979	0.0237	-0.0071	0.1975	-1.2303
HCOOH	-29.2555	0.8850	0.0766	-0.0347	0.1975	-1.3862
CO	-14.4495	0.1303	0.0013	-0.0003	0.1728	-1.1162
CO_2	-22.3071	0.3043	0.0477	-0.0249	0.1728	-1.1927
Adsorbates	**E0**	**ZPVE**	**H(v)**	**G(v)**	**H(t+r)**	**G(t+r)**
H*	-378.2528	0.1496	0.0473	-0.0233	-	-
H_2O*	-389.1202	0.6380	0.2282	-0.3360	-	-
OH*	-385.3310	0.3513	0.1486	-0.1457	-	-
O*	-381.4190	0.0719	0.0923	-0.0996	-	-
CH_3OH*	-404.8598	1.4032	0.3385	-0.4990	-	-
CH_2OH*	-400.4379	1.0812	0.2884	-0.3356	-	-
CH_3O*	-401.0583	1.0886	0.2828	-0.3775	-	-
CH_2O*	-396.8110	0.7664	0.2375	-0.2348	-	-
CHO*	-393.1484	0.4751	0.2014	-0.2076	-	-
CO*	-390.3079	0.1973	0.1844	-0.2705	-	-
H_2COOH*	-407.6010	1.2269	0.3543	-0.4484	-	-
HCOOH*	-404.2323	0.9152	0.3281	-0.4703	-	-
H_2COO*	-403.5296	0.9024	0.2949	-0.2996	-	-
COOH*	-400.3996	0.6138	0.2838	-0.3285	-	-
HCOO*	-401.0206	0.6201	0.2743	-0.3270	-	-
CO_2*	-397.0432	0.3216	0.2768	-0.5108	-	-
Transition States	**E0**	**ZPVE**	**H(v)**	**G(v)**	**H(t+r)**	**G(t+r)**
$CH_3OH^* \rightarrow CH_2OH^* + H^*$	-403.4980	1.2466	0.3122	-0.3459	-	-
$CH_3OH^* \rightarrow CH_3O^* + H^*$	-403.6057	1.1898	0.3126	-0.3879	-	-
$CH_3O^* \rightarrow CH_2O^* + H^*$	-400.1158	0.9330	0.2557	-0.2402	-	-
$CH_2OH^* \rightarrow CH_2O^* + H^*$	-399.3486	0.8899	0.2647	-0.2493	-	-
$CH_2O^* \rightarrow CHO^* + H^*$	-396.4811	0.6318	0.2161	-0.2037	-	-
$CHO^* \rightarrow CO^* + H^*$	-392.8491	0.4041	0.1929	-0.2490	-	-
$CH_2O^* + OH^* \rightarrow H_2COOH^*$	-407.1829	1.0881	0.3852	-0.4852	-	-
$H_2COOH^* \rightarrow H_2COO^* + H^*$	-406.3670	1.0025	0.3283	-0.3288	-	-
$H_2COOH^* \rightarrow HCOOH^* + H^*$	-407.0400	1.0635	0.3413	-0.3910	-	-

Table S1 Cont.: Electronic energy, ZPVE, and vibrational, translational, and rotational enthalpy and free energy at 573 K in eV.

Transition States	E0	ZPVE	H(v)	G(v)	H(t+r)	G(t+r)
HCOOH* → COOH* + H*	-403.2116	0.7642	0.3123	-0.3503	-	-
COOH* → CO_2* + H*	-398.9983	0.3796	0.2995	-0.3952	-	-
H_2COO* → HCOO* + H*	-403.0493	0.7583	0.2788	-0.2561	-	-
HCOOH* → HCOO* + H*	-403.4608	0.7508	0.3193	-0.4412	-	-
HCOO* → CO_2* + H*	-399.7838	0.4441	0.2940	-0.4048	-	-
H_2O* → H* + OH*	-387.9242	0.4647	0.1749	-0.1519	-	-
OH* → O* + H*	-383.4783	0.1915	0.1293	-0.1160	-	-
OH* + OH* → H_2O* + O*	-395.1121	0.7023	0.2508	-0.2667	-	-
$2H_2O$* → H_2O* + OH* + H*	-402.6465	1.1248	0.3614	-0.3771	-	-
CO* + OH* → COOH*	-400.1592	0.5467	0.2842	-0.3471	-	-
CO* + O* → CO_2*	-395.6368	0.2586	0.2243	-0.2658	-	-

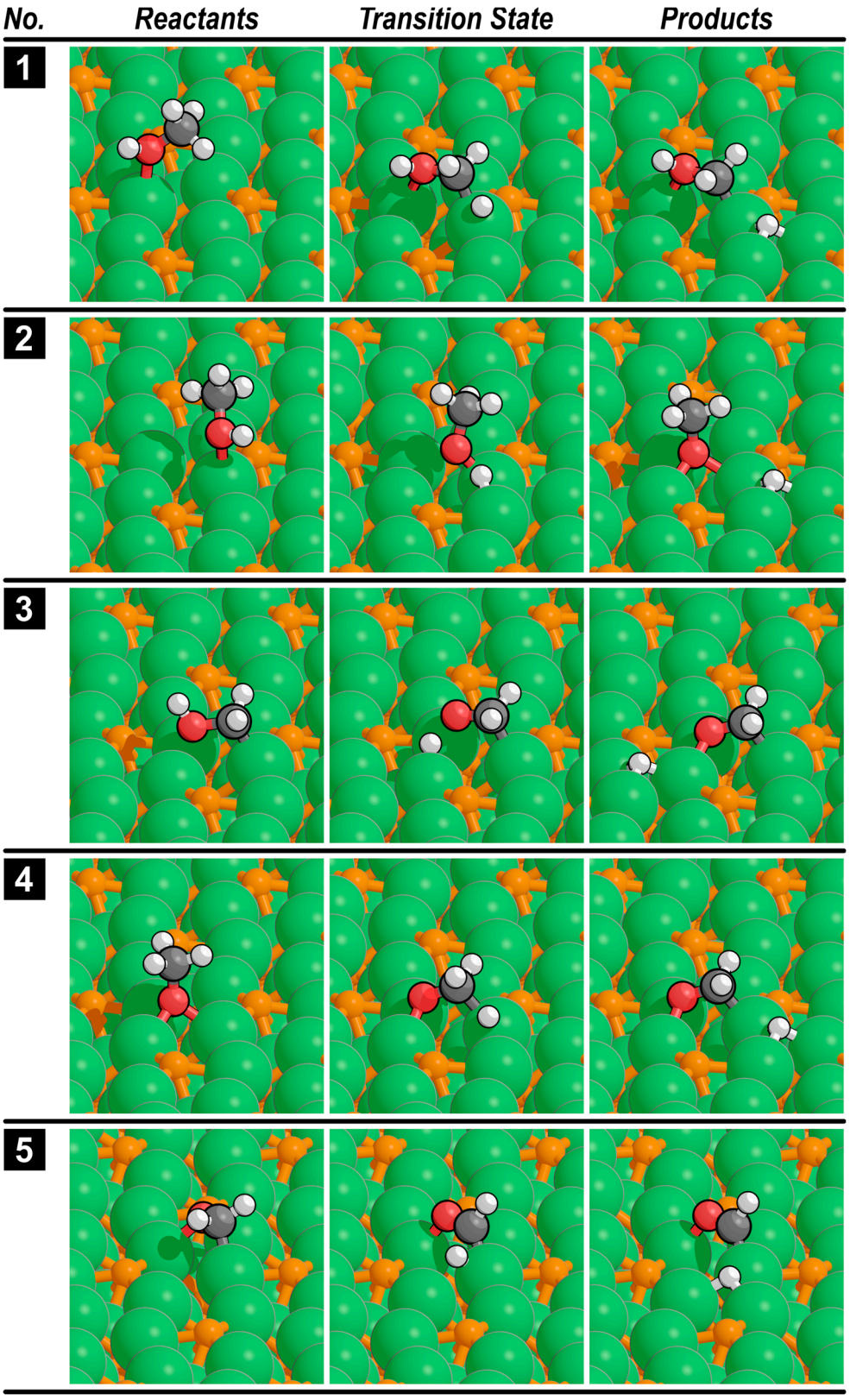


Figure S1. Reactants, transition state, and products structures for all reactions listed on Table 2.

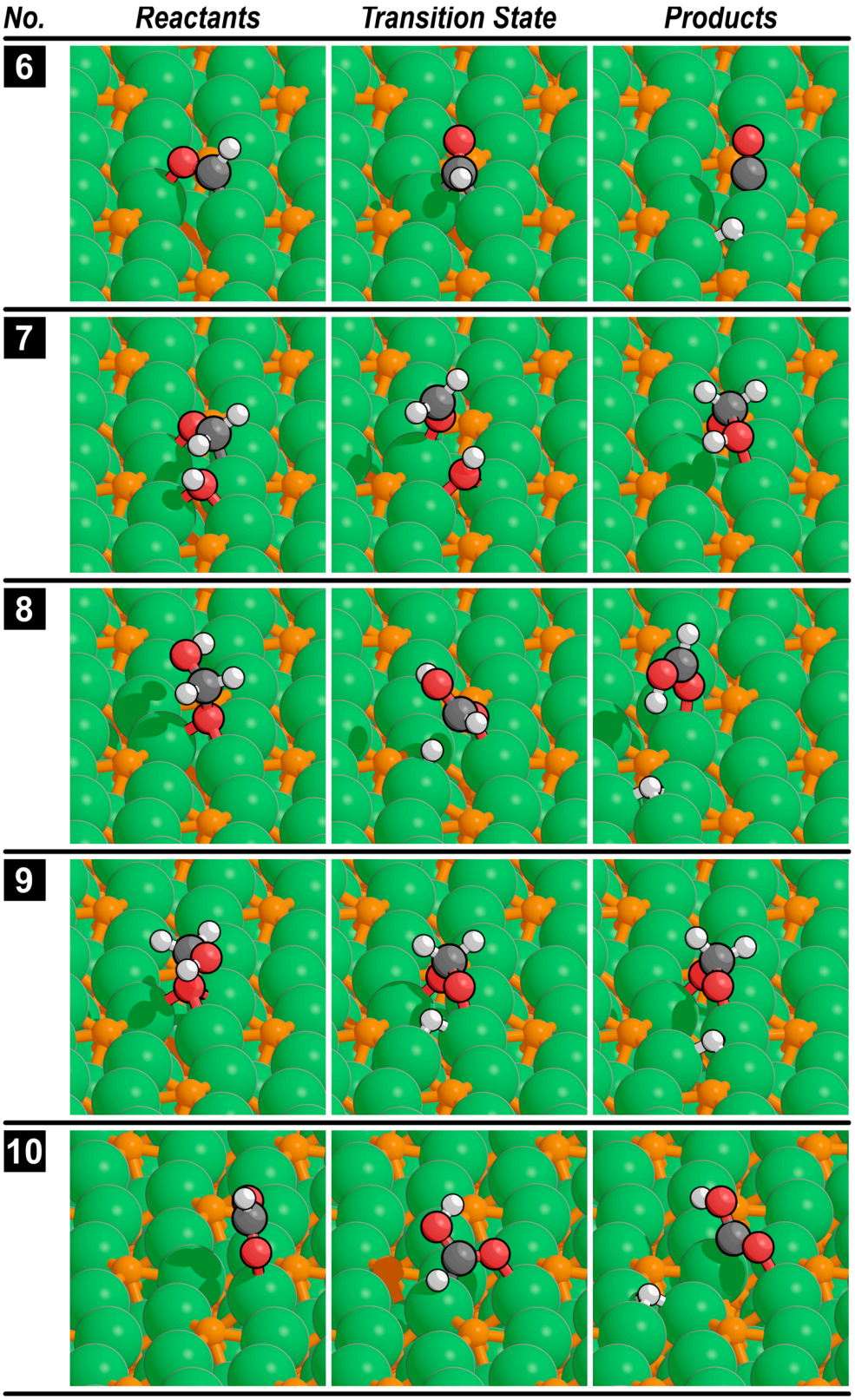
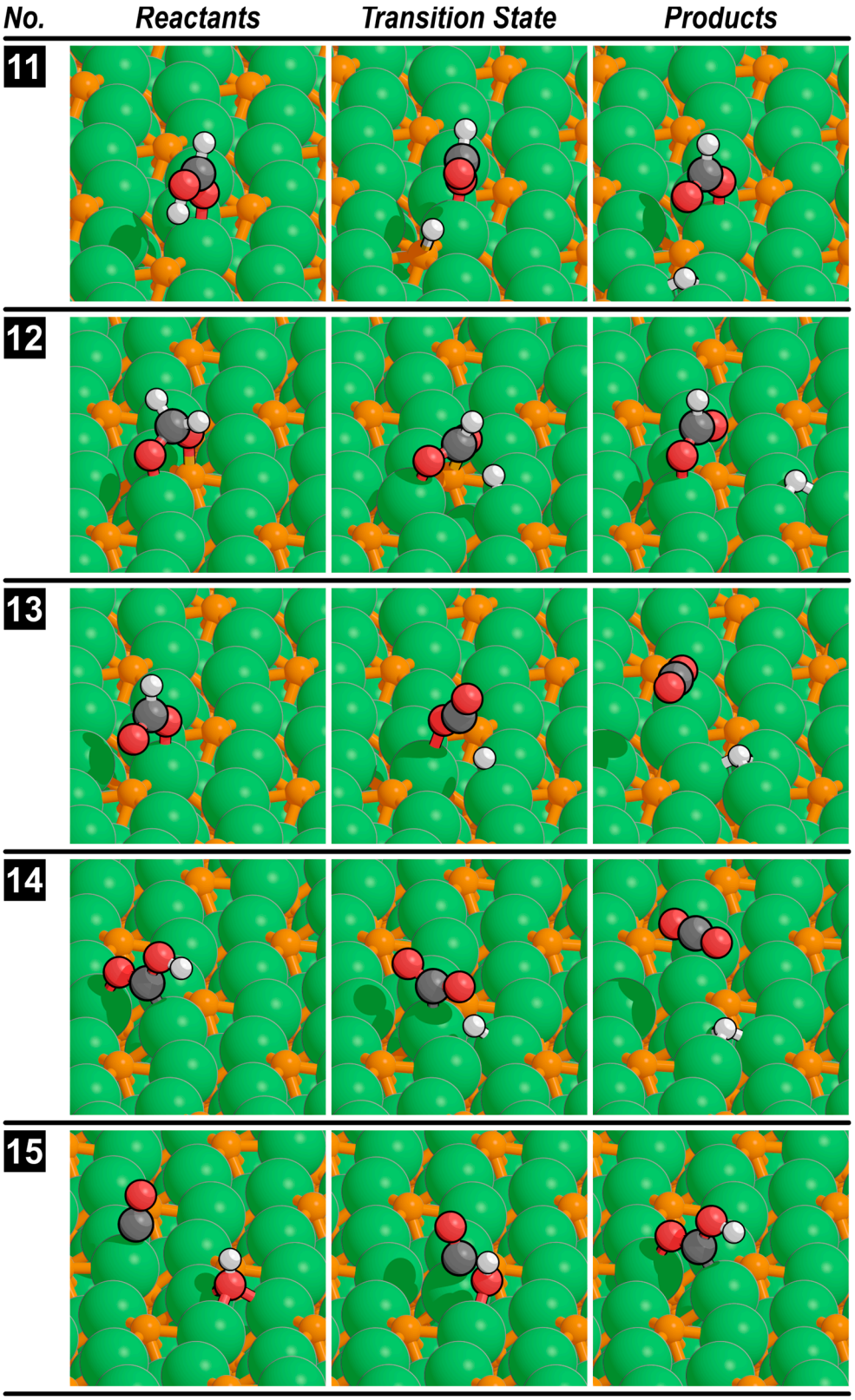


Figure S1 Cont. Reactants, transition state, and products structures for all reactions listed on Table 2.



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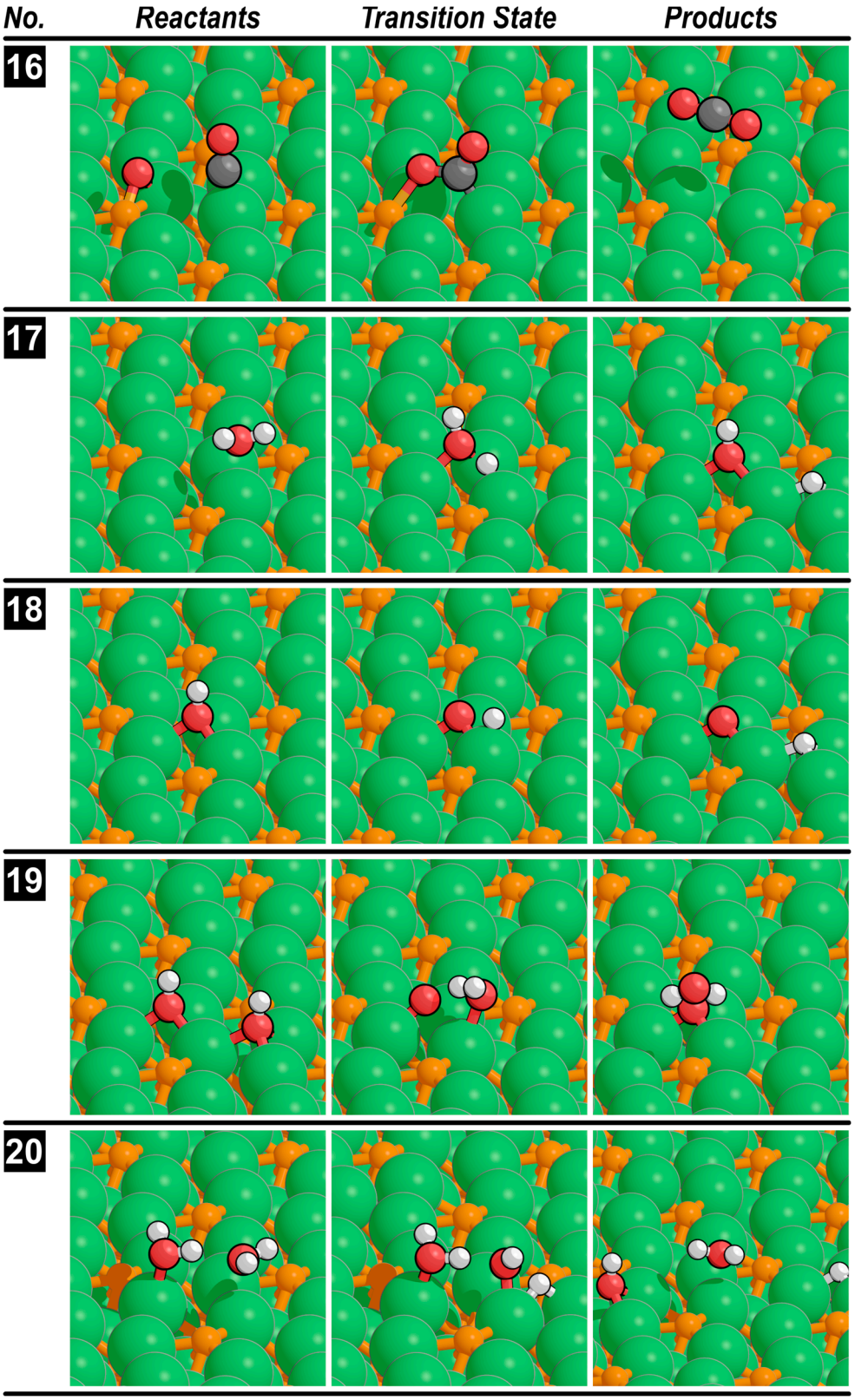

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