Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

The Mechanism of CO_2 Hydrogenation to CH_3OH on $MZrO_x$ (M = Ga, Cr) Solid-Solution Catalysts and Effects of Lattice Strain

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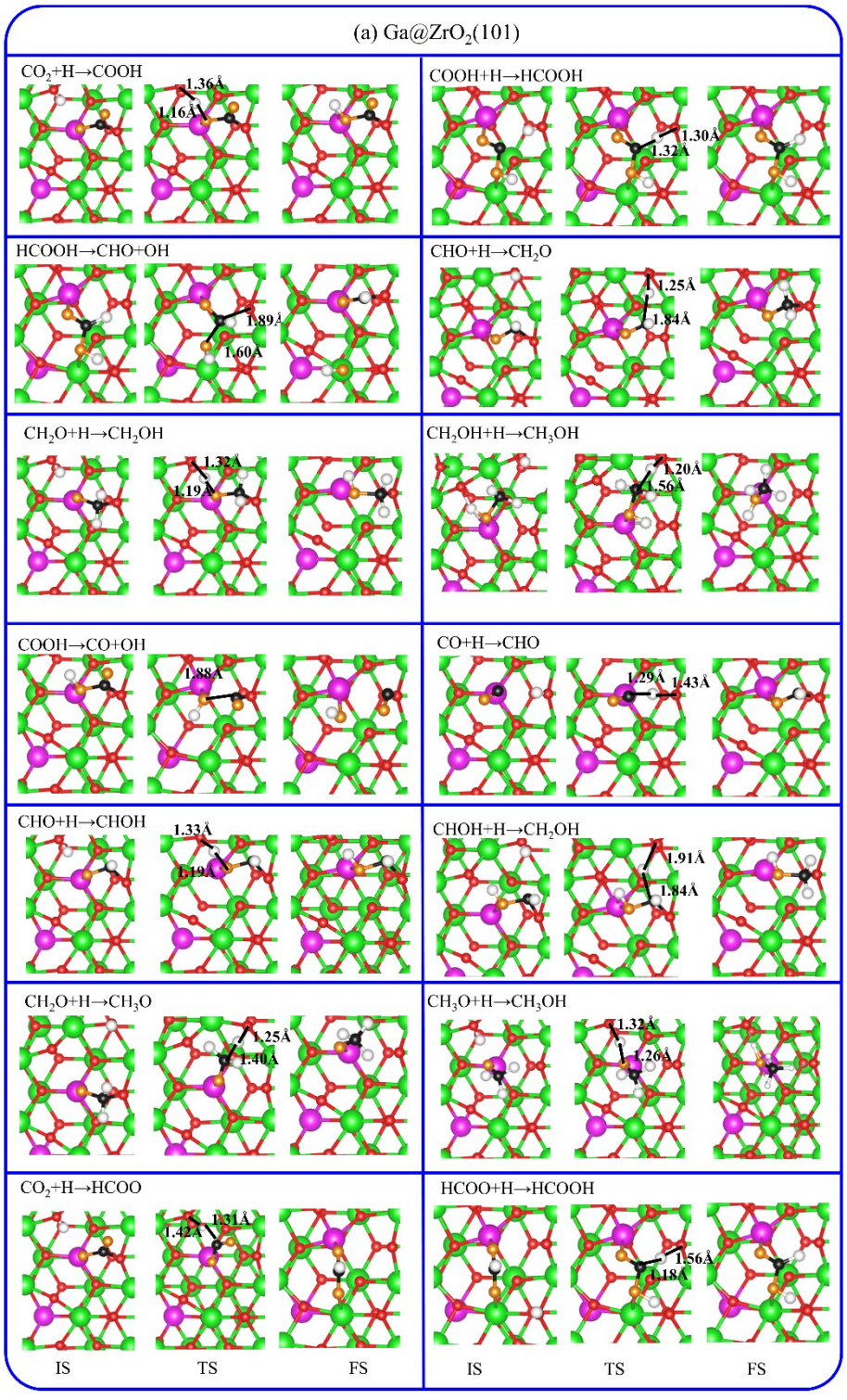
(a) Ga@ZrO2(101)
CO2+H→COOH
1.36Å
1.16Å
COOH+H→HCOOH
1.30Å
1.32Å
HCOOH→CHO+OH
1.89Å
1.60Å
CHO+H→CH2O
1.25Å
1.84Å
CH2O+H→CH2OH
1.32Å
1.19Å
CH2OH+H→CH3OH
1.20Å
1.56Å
COOH→CO+OH
1.88Å
CO+H→CHO
1.29Å
1.43Å
CHO+H→CHOH
1.33Å
1.19Å
CHOH+H→CH2OH
1.91Å
1.84Å
CH2O+H→CH3O
1.25Å
1.40Å
CH3O+H→CH3OH
1.32Å
1.26Å
CO2+H→HCOO
1.42Å
1.31Å
HCOO+H→HCOOH
1.56Å
1.18Å
IS
TS
FS
IS
TS
FS

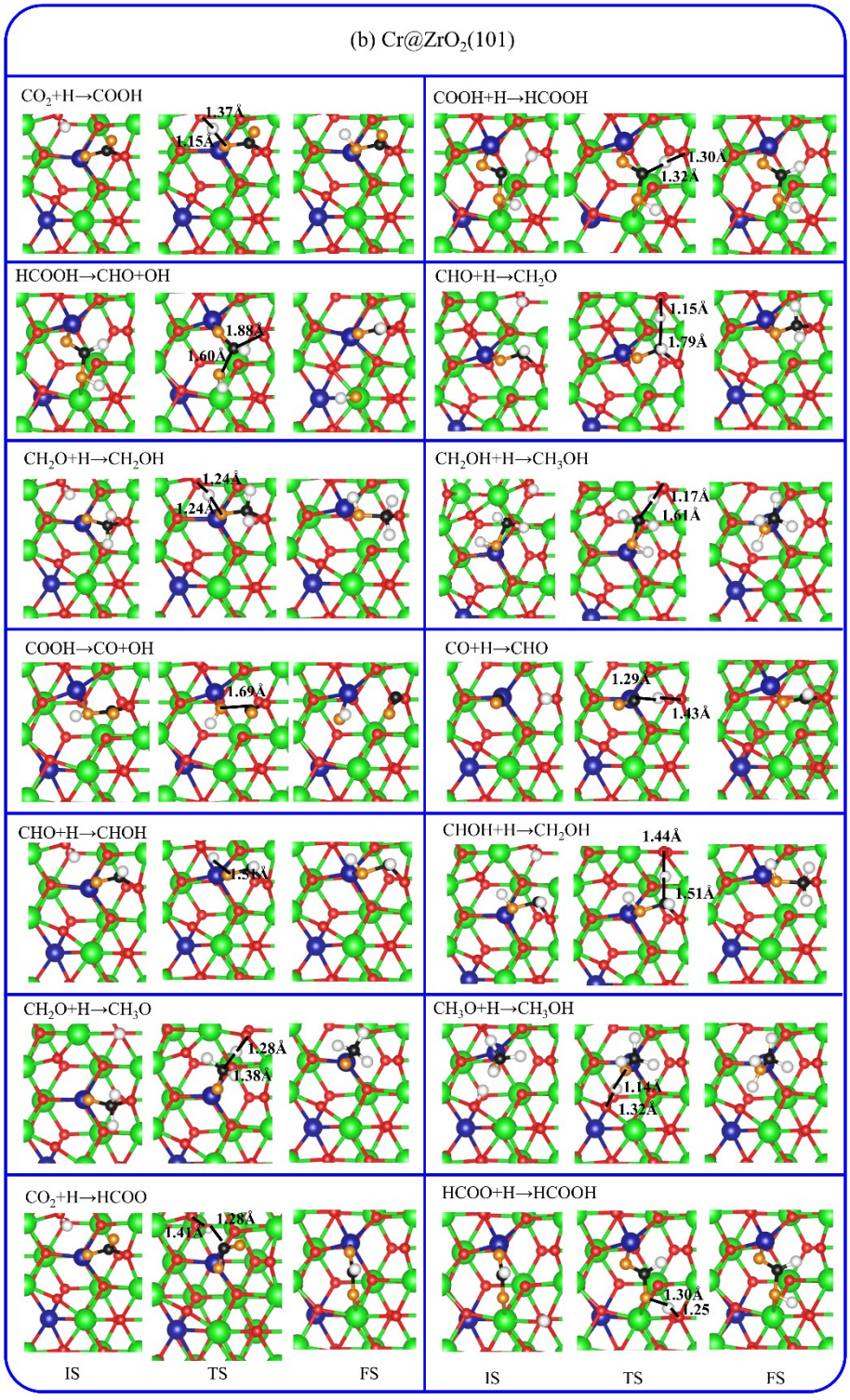

Figure S1. The initial state (IS), transition state (TS) and final state (FS) of elementary steps involved in CO_2 hydrogenation to methanol on the $GaZrO_x(101)$ (a) and $CrZrO_x(101)$ (b) surfaces.

Table S1. The barrier (E_a) and reaction heat (ΔH) without zero-point energy corrections of elementary steps involved in CO_2 hydrogenation to methanol on the $MZrO_x(101)$ (M = Ga, Cr) surfaces with strain from -1% to 1% [a].

Elementary step	E_a/eV (-1%/0/1%)		ΔH/eV (-1%/0/1%)	
	$GaZrO_x(101)$	$CrZrO_x(101)$	$GaZrO_x(101)$	$CrZrO_x(101)$
CO*+H*→CHO*+*	0.60/0.62/2.13	1.66/1.86/2.75	-0.25/-0.40/-0.49	-0.45/-0.54/-0.61
CHOH*+H*→CH_2OH*+*	1.22/1.68/1.49	0.94/0.64/1.08	-1.38/-1.20/-1.21	-1.25/-1.02/-1.05
CH_2OH*+H*→CH_3OH*+*	0.52/0.22/0.75	0.78/1.04/1.01	-2.51/-2.34/-2.05	-2.29/-2.21/-1.95
COOH*+H*→HCOOH*+*	0.35/0.25/0.75	0.72/0.62/1.01	0.00/0.08/0.47	0.05/-0.15/0.22
CH_2O*+H*→CH_3O*+*	1.29/1.27/2.40	2.46/2.13/2.63	0.29/0.32/0.49	1.51/0.28/0.57
CHO*+H*→CH_2O*+*	0.67/0.53/0.68	0.91/0.52/1.03	-1.81/-1.70/-1.70	-1.49/-1.39/-1.31
CO_2*+H*→HCOO*+*	1.41/1.40/1.50	1.66/1.04/2.76	0.69/0.76/0.55	-0.26/-0.22/-0.01
CO_2*+H*→COOH*+*	0.70/0.81/0.89	0.93/0.70/1.30	0.68/0.68/0.78	0.60/0.59/0.79
CHO*+H*→CHOH*+*	0.26/0.81/0.98	0.98/0.84/2.17	0.12/0.24/0.80	0.54/0.64/1.37
CH_2O*+H*→CH_2OH*+*	0.84/0.63/0.97	0.85/0.44/0.90	0.32/0.41/0.39	0.43/0.28/0.44
CH_3O*+H*→CH_3OH*+*	0.23/0.38/0.50	1.36/0.48/1.12	0.14/0.17/0.30	-1.81/0.27/0.09
H*+HCOO*→HCOOH*+*	2.19/1.85/2.05	1.79/1.43/2.03	1.58/1.65/2.11	1.58/1.42/1.84
H*+OH*→H_2O*+*	1.09/0.61/1.32	1.09/0.72/0.70	0.15/0.24/0.40	0.17/0.24/0.34
HCOOH*+*→CHO*+OH*	0.54/0.75/0.69	1.66/1.38/1.60	-1.20/-1.11/-1.51	-1.25/-1.08/-1.19
COOH*+*→CO*+OH*	1.64/1.16/1.38	1.99/0.96/2.34	-0.25/-0.14/-0.28	1.11/0.24/1.15
H_2*+*→2H*	1.22/1.25/0.96	1.53/1.42/1.64	0.82/1.24/0.37	0.87/0.79/0.72

a: The data of each column represents the result at -1%, 0 and 1% strain respectively.

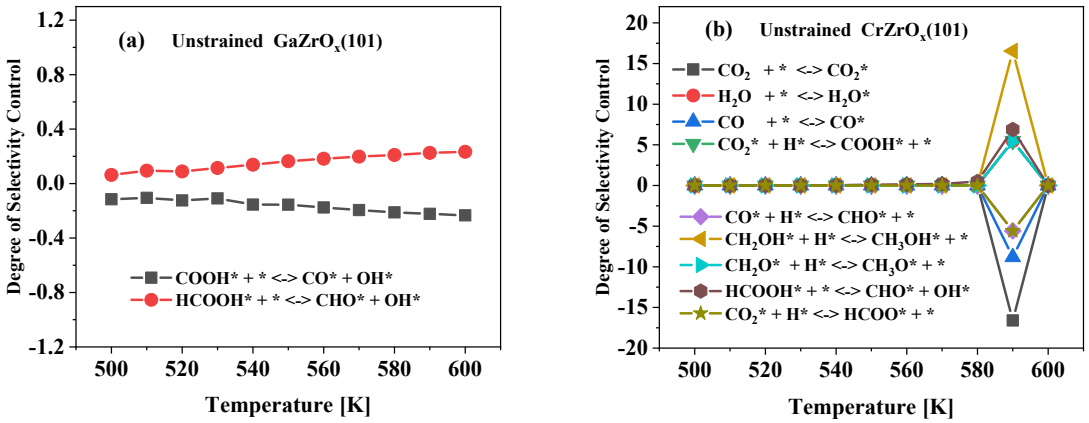

Figure S2. Degree of selectivity control (DSC) of methanol as a function of temperature on the $GaZrO_x(101)$ (a) and $CrZrO_x(101)$ (b) surface with strain from -1% to 1%. Simulation conditions: CO_2:H_2 = 1:3, p = 20 bar. Only elementary steps with the DSC coefficients greater than 0.2 (absolute values) are shown.

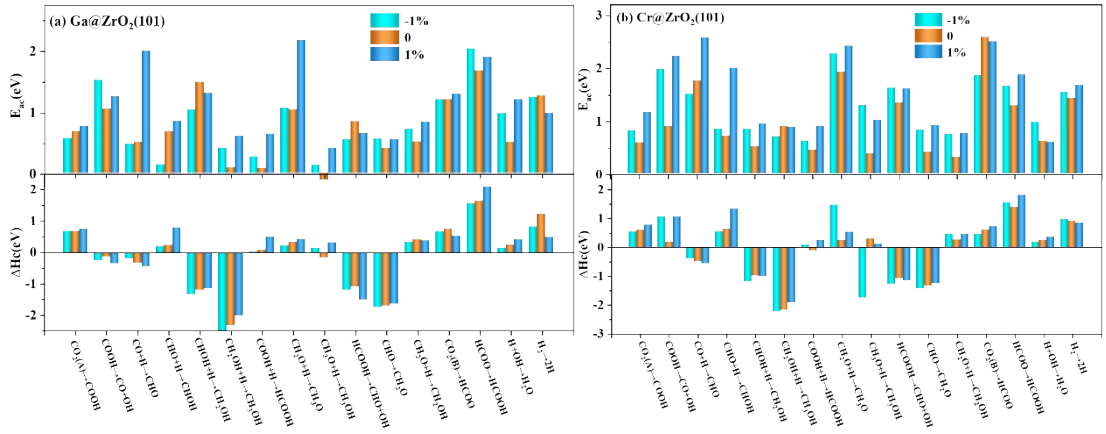

Figure S3. Zero-point corrected barriers (E_{ac}) and reaction heats (ΔHc) of elementary steps involved in CO_2 hydrogenation to methanol over the $GaZrO_x(101)$ ((a), (b)) and $CrZrO_x(101)$ ((c), (d)) surfaces with strain from -1% to 1%.

Table S2. The bond length (*d, Å*) of the initial and transition states of the step of HCOOH → CHO + OH on $MZrO_x(101)$ (M = Ga, Cr) surfaces. All unit are in Å. For the atomic numbering, please see Figure 1c in the body text.

	$GaZrO_x(101)$						$CrZrO_x(101)$					
	IS			TS			IS			TS		
M-O_M	2.2859	2.0506	2.3467	1.9168	1.9832	2.0009	2.2364	2.1264	2.1333	1.9767	1.9834	2.0033
Zr-O_Z	2.5760	2.6399	2.7454	2.2908	2.3001	2.3211	2.5506	2.6146	2.5189	2.2752	2.2999	2.3229
C-O_M	1.2120	1.2578	1.2081	1.2871	1.2532	1.2549	1.2109	1.2396	1.2303	1.2439	1.2531	1.2655
C-O_Z	1.3573	1.3666	1.3539	1.5431	1.6005	1.6162	1.3598	1.3500	1.3409	1.5465	1.6004	1.6164
C-H_2	1.1015	1.1778	1.1070	1.0922	1.0983	1.0938	1.1037	1.1158	1.1008	1.0884	1.0981	1.1091
O_Z-H_1	0.9798	1.0345	0.9800	0.9953	0.9881	0.9866	1.1037	1.0235	1.0698	0.9840	0.9880	0.9978
C-O_1	---	---	---	1.6528	1.8851	1.8579	---	---	---	1.9342	1.8846	1.9034
H_2-O_1	3.7242	1.5652	3.7725	2.0301	2.1236	2.1236	3.6934	1.8142	2.5375	2.1174	2.1234	2.1446
O_2-H_1	2.8582	1.6821	3.0432	1.8640	2.6800	2.7046	2.1602	1.7786	1.5788	2.6431	2.6796	2.7063

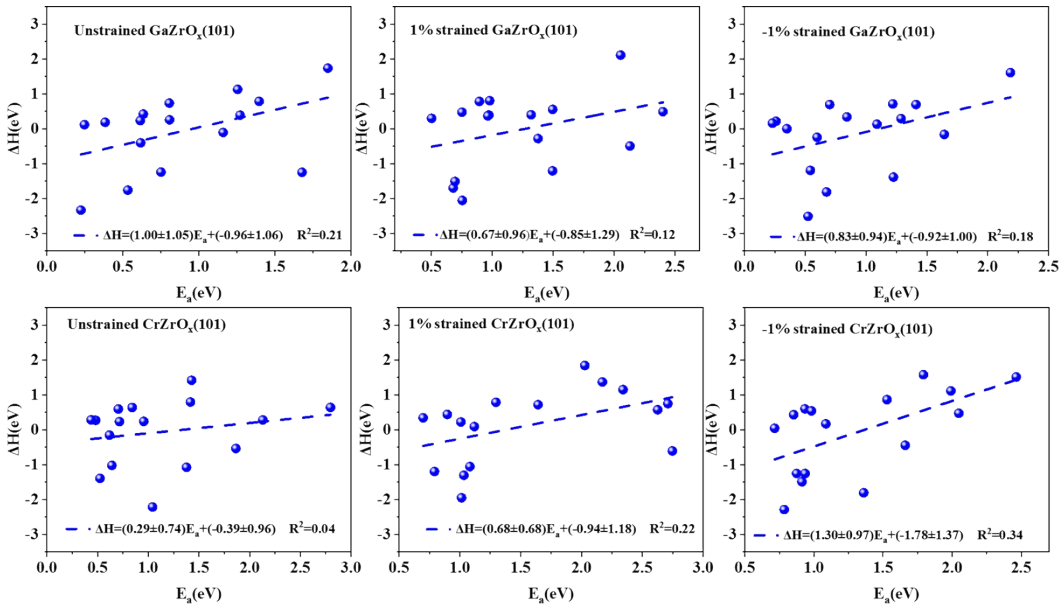

Figure S4. BEP relationship on $MZrO_x(101)$(M = Ga, Cr) surfaces with strain from -1% to 1%.

Table S3. The absolute errors (AEs, eV) between predicted barrier by BEP relationship between the oxygen hydrogenation or carbon hydrogenation elementary steps and calculated barrier by DFT on $MZrO_x(101)$ (M = Ga, Cr) with strain from -1% to 1%.

	Absolute Errors(AEs)	$GaZrO_x(101)$			$CrZrO_x(101)$		
		-1%	0	1%	-1%	0	1%
C-H bond	CO*+H*→CHO*+*	0.78	0.41	0.51	0.40	0.28	0.87
	CHOH*+H*→CH_2OH*+*	1.09	1.26	0.73	0.13	0.16	0.08
	CH_2OH*+H*→CH_3OH*+*	1.40	1.21	1.00	0.93	1.33	0.93
	COOH*+H*→HCOOH*+*	1.31	1.22	1.53	1.50	1.05	1.25
	CH_2O*+H*→CH_3O*+*	0.51	0.70	0.26	0.36	0.33	0.40
	CHO*+H*→CH_2O*+*	0.88	0.87	0.59	0.33	0.12	0.29
	CO_2(B)*+H*→HCOO*+*	0.77	1.00	1.03	0.06	0.18	0.51
O-H bond	CO_2(A)*+H*→COOH*+*	0.29	0.19	0.23	0.44	0.10	0.04
	CHO*+H*→CHOH*+*	0.11	0.29	0.16	0.36	0.02	0.24
	CH_2O*+H*→CH_2OH*+*	0.16	0.06	0.24	0.31	0.10	0.09
	CH_3O*+H*→CH_3OH*+*	0.07	0.10	0.18	2.13	0.04	0.47
	H*+HCOO*→HCOOH*+*	0.21	0.03	0.29	1.08	0.06	0.38
	H*+OH*→H_2O*+*	0.53	0.10	0.62	0.05	0.28	0.19

Table S4. The slope, intercept (eV), correlation (R^2) of BEP relationship between the oxygen hydrogenation or carbon hydrogenation elementary steps on $GaZrO_x(101)$/$CrZrO_x(101)$ surfaces with strain from -1% to 1%, the mean/maximum absolute error(eV) between predicted value by BEP and calculated value by DFT.

C-H bond	$GaZrO_x(101)$			$CrZrO_x(101)$		
	-1%	0	1%	-1%	0	1%
slope	1.17±2.28	0.78±1.64	0.78±1.24	1.49±0.99	0.76±0.73	0.74±0.79
intercept	-1.72±2.17	-1.30±1.66	-1.64±1.90	-2.52±1.48	-1.68±1.16	-1.78±1.52
R^2	0.17	0.15	0.24	0.65	0.47	0.41
mean absolute error	0.96	0.95	0.81	0.53	0.49	0.62
maximum absolute error	1.40	1.26	1.53	1.50	1.33	1.25
O-H bond	$GaZrO_x(101)$			$CrZrO_x(101)$		
	-1%	0	1%	-1%	0	1%
slope	0.67±0.42	1.11±0.33	1.09±0.68	0.40±3.14	1.19±0.40	0.99±0.51
intercept	-0.07±0.46	-0.34±0.32	-0.43±0.82	-0.21±3.81	-0.34±0.33	-0.54±0.75
R^2	0.72	0.92	0.72	0.02	0.90	0.79
mean absolute error	0.23	0.13	0.29	0.73	0.10	0.24
maximum absolute error	0.53	0.29	0.62	2.13	0.28	0.47

Table S5. The absolute errors (AEs, eV) between predicted barrier by TSS relationship between the oxygen hydrogenation or carbon hydrogenation elementary steps and calculated barrier by DFT on $MZrO_x(101)$ (M = Ga, Cr) with strain from -1% to 1%.

	Absolute Errors(AEs)	$GaZrO_x(101)$			$CrZrO_x(101)$		
		-1%	0	1%	-1%	0	1%
C-H bond	CO*+H*→CHO*+*	0.39	0.33	0.35	0.16	0.26	0.68
	CHOH*+H*→CH_2OH*+*	0.53	0.94	0.53	0.01	0.03	0.05
	CH_2OH*+H*→CH_3OH*+*	0.43	0.67	0.80	0.94	0.97	1.25
	COOH*+H*→HCOOH*+*	0.30	0.46	0.02	0.40	0.43	0.42
	CH_2O*+H*→CH_3O*+*	0.27	0.32	0.62	0.97	0.59	0.74
	CHO*+H*→CH_2O*+*	0.06	0.23	0.32	0.38	0.70	0.56
	CO_2*+H*→HCOO*+*	0.37	0.43	0.351	0.57	1.27	0.76
O-H bond	CO_2*+H*→COOH*+*	0.18	0.17	0.12	0.03	0.21	0.17
	CHO*+H*→CHOH*+*	0.60	0.02	0.10	0.17	0.14	0.78

	$CH_2O^*+H^*\rightarrow CH_2OH^*+^*$	0.17	0.08	0.06	0.25	0.21	0.35
	$CH_3O^*+H^*\rightarrow CH_3OH^*+^*$	0.85	0.58	0.79	0.36	0.35	0.29
	$H^*+HCOO^*\rightarrow HCOOH^*+^*$	1.07	0.85	0.67	0.37	0.43	0.47
	$H^*+OH^*\rightarrow H_2O^*+^*$	0.03	0.34	0.03	0.28	0.22	0.79

Table S6. The slope, intercept (eV), correlation (R^2) of TSS relationship between the oxygen hydrogenation or carbon hydrogenation elementary steps on $GaZrO_x(101)$/$CrZrO_x(101)$ surfaces with strain from -1% to 1%, the mean/maximum absolute error(eV) between predicted value by TSS and calculated value by DFT.

C-H bond	$GaZrO_x(101)$			$CrZrO_x(101)$		
	-1%	0	1%	-1%	0	1%
slope	1.21±0.43	1.13±0.60	1.51±0.52	1.34±0.72	1.48±0.77	1.52±0.86
intercept	-1.64±1.66	-1.34±2.34	-3.34±2.04	-2.78±3.08	-3.46±3.43	-4.13±3.99
R^2	0.86	0.74	0.87	0.74	0.75	0.71
mean absolute error	0.34	0.48	0.43	0.49	0.61	0.64
maximum absolute error	0.53	0.94	0.80	0.94	1.27	1.25
O-H bond	$GaZrO_x(101)$			$CrZrO_x(101)$		
	-1%	0	1%	-1%	0	1%
slope	0.84±0.44	0.90±0.32	0.85±0.30	0.84±0.25	0.82±0.29	0.85±0.55
intercept	-0.06±2.37	-0.34±1.72	-0.33±1.60	-0.35±1.32	0.22±1.63	-0.50±3.24
R^2	0.79	0.89	0.89	0.92	0.89	0.70
mean absolute error	0.48	0.34	0.29	0.24	0.26	0.47
maximum absolute error	1.07	0.85	0.79	0.37	0.43	0.79