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Insight into methanol oxidation mechanisms on RuO_2(100) under aqueous environment by DFT calculations

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Supporting information

Table S1. Reaction barriers (E_a, in eV) and thermodynamic data (ΔE, in eV) in the elementary steps of methanol electrooxidation at the aqueous interface and in vacuum respectively.

surface reactions	**aqueous**		**vacuum**	
	E_a	ΔE	E_a	ΔE
$CH_3OH^* + O_{br} \rightarrow CH_3O^* + O_{br}H^*$	0.09	0	0.17	0.06
$CH_3O^* + O_{br} \rightarrow HCHO^* + O_{br}H^*$	0.57	-0.57	0.59	-0.67
$HCH(OH)_2^* + O_{br} \rightarrow HCHOOH^* + O_{br}H^*$	0.06	0.03	0.08	0.03
$HCHOOH^* + O_{br} \rightarrow HCOOH^* + O_{br}H^*$	0.47	-1.36	0.59	-1.99
$HCOOH^* + O_{br} \rightarrow$ mono-$HCOO^* + O_{br}H^*$	/	-0.53	/	0.13
$HCOOH^* + O_{br} \rightarrow$ bi-$HCOO^* + O_{br}H^*$	/	-0.21	/	-0.71
mono-$HCOO^* + O_{br} \rightarrow CO_2^* + O_{br}H^*$	0.54	-0.42	0.54	-1.44
bi-$HCOO^* + O_{br} \rightarrow CO_2^* + O_{br}H^*$	1.10	-0.75	1.11	-0.60

Table S2. Adsorption energies (in eV) of the reactants at the aqueous interface and in vacuum respectively.

surface species	**aqueous**	**vacuum**
CH_3OH^*	-0.33	-1.06
$HCHO^*$	-0.2	-0.71
$HCH(OH)_2^*$	-0.4	-0.9
$HCOOH^*$	-0.53	-0.98
CO_2^*	0.1	-0.18

Table S3. Bader charges analysis (in e) of surface adsorbed species at the aqueous $RuO_2(100)$ interface and in vacuum respectively.

surface species	aqueous	vacuum
CH_3OH^*	+0.11	+0.1
CH_3O^*	-0.29	-0.27
HCHO*	+0.09	+0.08
$HCH(OH)_2^*$	+0.09	+0.13
HCHOOH*	-0.40	-0.28
HCOOH*	+0.12	+0.07
mono-HCOO*	-0.57	-0.40
bi-HCOO*	-0.51	-0.47
CO_2^*	-0.01	0

Computational details for HCHO hydration

A periodically repeated cubic unit cell with an edge length of 10 Å was used to model this system for HCHO hydration to $HCH(OH)_2$. 32 water molecules and 1 HCHO molecules were added into the cubic cell (Fig. S1). Constrained ab initio molecular dynamics method and thermodynamic integration were combined to compute the free energy of aqueous reactions[1-3]. The cut-off energy was set as 450 eV and a gamma k-point sampling was used. The MD simulations were performed within the canonical (NVT) ensemble at a constant temperature of 300 K. For each state (per 0.1 Å) we performed MD simulation for 5 ps (1 fs per step, 5000 steps) until the interatomic forces were converged. We selected the samples from the last 1 ps (1000 samples) of each MD simulation to do the average of the interatomic force (free-energy gradient). The free energy profile was presented in Fig. S2.

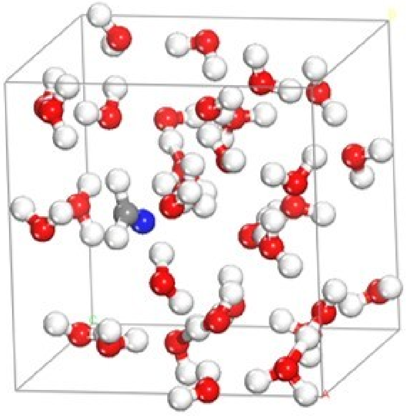

Fig S1. Model of a HCHO molecule solvated in a water box with 32 water molecules.

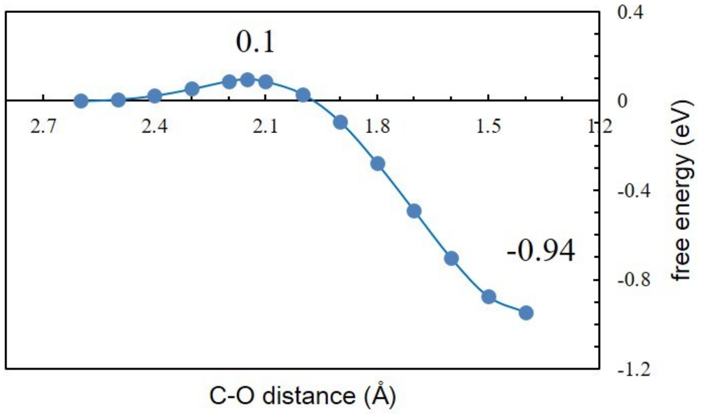

Fig S2. Free energy profile for HCHO hydration in aqueous solution.

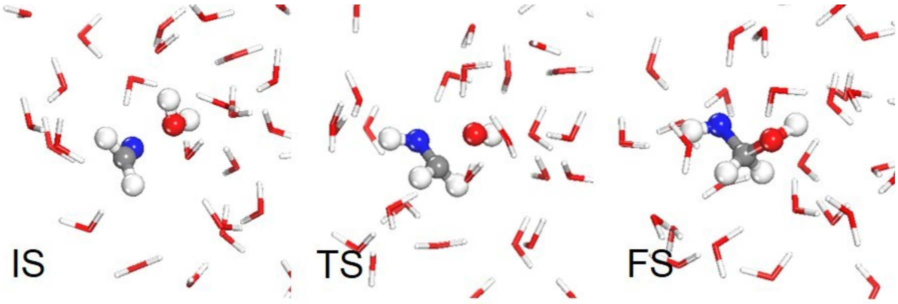

Fig S3. Initial, transition and final states for HCHO hydration obtained from molecular simulations.

Reference

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3 T. Bucko, *J. Phys.: Condens. Matter,* 2008, **20,** 064211.