Supporting Information

Perimeter Power: Unveiling the Role of Ni-TiO_2 Interface Sites in Enhancing Acetic Acid Ketonization Catalysis

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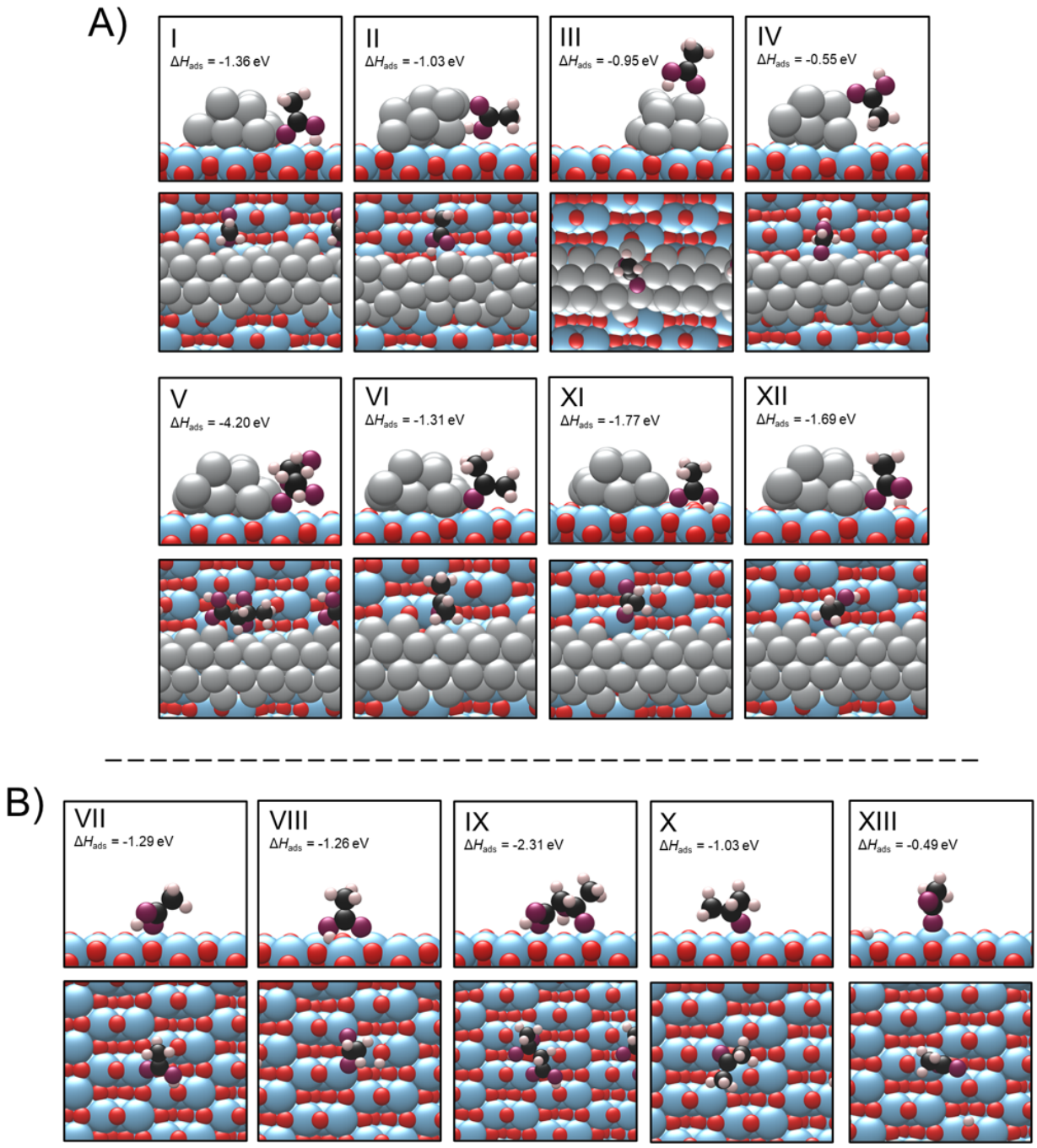

Figure S1: DFT-calculated adsorption modes for A) $Ni_{20}/TiO_2(101)$ and B) pristine $TiO_2(101)$. Adsorption enthalpies (ΔH_{ads}) were calculated at 623 K and 2 kPa acetic acid. Adsorption enthalpies for molecular and dissociated acetic acid are referenced to acetic acid in the gas phase, whereas acetone and CH_2COOH-CH_3COOH (C-C coupling product) are referenced to their respective gaseous structures. Pink, black, light red, dark red, blue, and gray spheres represent H, C, O (TiO_2), O (CH_3COOH), Ti, and Ni atoms, respectively.

Table S1: DFT-calculated vibrational frequencies for $Ni_{20}/TiO_2(101)$. Vibrational modes labeled ν and δ denote stretching and deformations, respectively.

Assignment	**Vibrational Frequency [cm^{-1}]**			
		CH_3COOH (molecular)		
	Structure I	**Structure II**	**Structure III**	**Structure IV**
ν(OH)	2617	2253		2886
δ_s(CH_3)	1330, 1350, 1410	1335, 1384, 1406	1318, 1344, 1392	1332, 1421, 1436
ν_s(OCO)	1400	1393	1432	1375
ν_a(OCO)	1494			
ν(C=O)	1596	1749	1623	
ν(CH)	2960, 3031, 3106	2858, 3020, 3110	2869, 3008, 3101	2989, 3066, 3107

	CH_2COOH-CH_3COOH **Structure V**	**$(CH_3)_2CO$** **Structure VI**	**CH_3COO + H (O,O)** **Structure XI**	**CH_3COO + H (O)** **Structure XII**
ν(OH)	3572, 3612			
ν(C-OH)	1321			
δ_s(CH_2 or CH_3)	1354, 1362, 1425, 1443	1301, 1342, 1369, 1421, 1437	1325, 1379, 1401, 1422	1337, 1390, 1413
ν_a(OCO)	1414		1490	1543
ν(C=O)	1642	1513		
ν(CH)	2862, 2931, 3035, 3067, 3077	2748, 2870, 2944, 3022, 3082, 3094	2967, 3043, 3105	2931, 3007, 3091

Table S2: DFT-calculated vibrational frequencies for pristine $TiO_2(101)$. Vibrational modes labeled ν and δ denote stretching and deformations, respectively.

Assignment	**Vibrational Frequency [cm^{-1}]**		
	CH_3COOH **Structure VII**	**CH_3COO + H (O,O)** **Structure VIII**	**CH_2COOH-CH_3COOH** **Structure IX**
ν(OH)	2438		
ν(C-OH)	1311		1302
δ_s(CH_2 or CH_3)	1342, 1407, 1428	1330, 1417, 1431	1327, 1375, 1412, 1436
ν_s(OCO)		1380	
ν_a(OCO)	1483	1482	1449
ν(C=O)	1610		1637
ν(CH)	2991, 3066, 3113	2993, 3062, 3108	3000, 3007, 3083, 3105, 3121

	$(CH_3)_2CO$ **Structure X**	**CH_3COO + H (O)** **Structure XIII**
δ_s(CH_2 or CH_3)	1320, 1338, 1402, 1416, 1436	1338, 1414, 1426
ν_a(OCO)		1725
ν(C=O)	1674	
ν(CH)	2958, 2974, 3040, 3046, 3097, 3104	2990, 3059, 3099

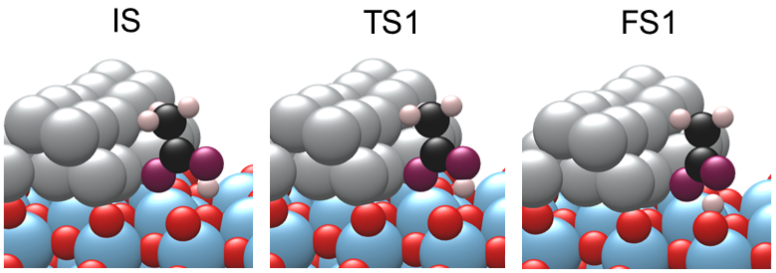

Figure S2: Initial (IS), transition (TS), and final (FS) states for CH_3COOH dehydrogenation to produce CH_3COO (O,O) over $Ni_{20}/TiO_2(101)$. Pink, black, light red, dark red, blue, and gray spheres represent H, C, O (TiO_2), O (CH_3COOH), Ti, and Ni atoms, respectively.

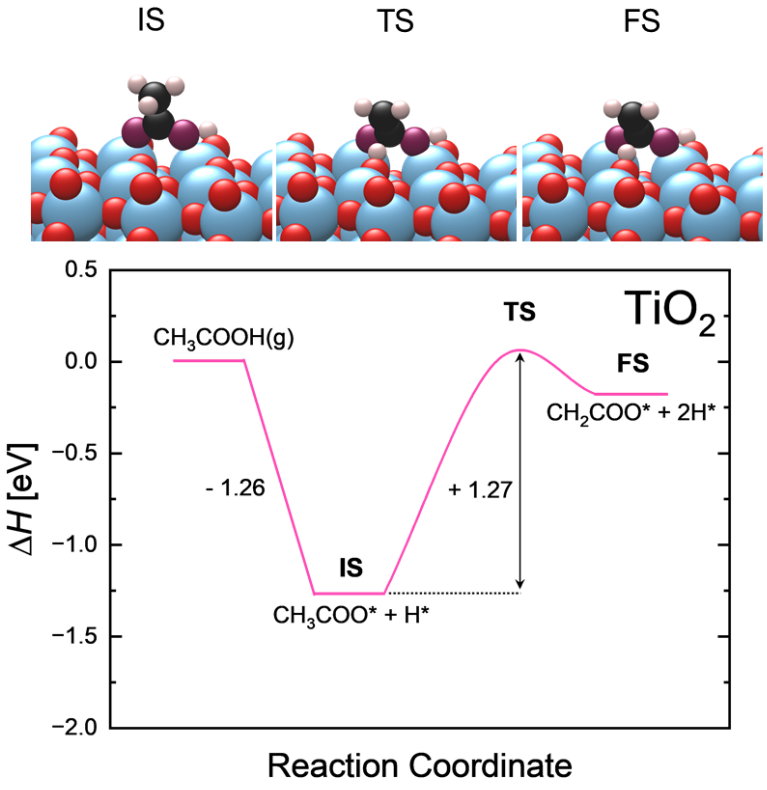

Figure S3: Potential energy surface for CH_3COO (O,O) C-H bond scission over pristine anatase $TiO_2(101)$ (623 K, 2 kPa acetic acid). Pink, black, light red, dark red, blue, and gray spheres represent H, C, O (TiO_2), O (CH_3COOH), Ti, and Ni atoms, respectively.