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

Investigation of Solvent Effects on the Hydrodeoxygenation of Guaiacol over Ru Catalysts

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Table S1. Kamlet and Taft's solvatochromic parameters; polarizability (π^*), hydrogen-bond donor (α)and acceptor (β), and normalized polarity (E_T^N) derived from the solvatochromism of pyridinium N-phenolate betaine for solvents employed in the HDO of guaiacol over Ru(0001) model surface.

Solvents	π^*	α	β	E_T^N
Water	1.09	1.17	0.47	1.000
1-Butanol	0.47	0.84	0.84	0.586
Diethyl ether	0.24	0.00	0.47	0.117
n-Hexane	-0.11	0.00	0.00	0.009

Table S2. Lateral interaction parameters employed in the microkinetic model for the HDO of guaiacol over a Ru(0001) model surface.

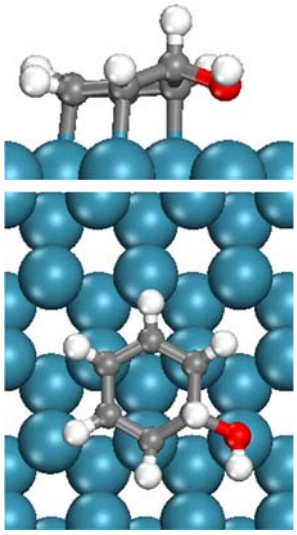
Adsorbate pairs	Lateral interaction (eV)
H-H	0.150(θ_H - 0.100)
CO-CO	1.686(θ_{CO} - 0.092)
H-CO	(0.229+2.140$\sqrt{\theta_{CO}\theta_H}$) θ_{CO}
H-Phenoxy	(-1.124+16.565$\sqrt{\theta_{Phenoxy}\theta_H}$) $\theta_{Phenoxy}$
CO-Phenoxy	(0.851+11.255$\sqrt{\theta_{Phenoxy}\theta_{CO}}$) $\theta_{Phenoxy}$

Table S3: Free energies of reaction (in eV) in the limit of zero coverage at different reaction temperatures under vapor phase reaction conditions for the phenol hydrogenation over Ru(0001).

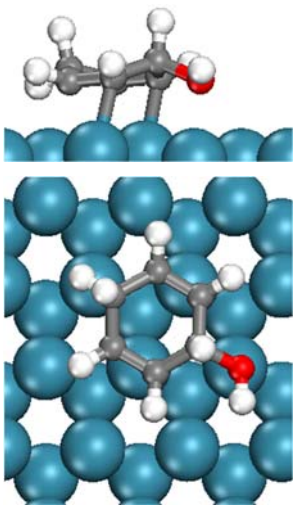
ID	Reaction	Vapor phase, ΔG_{rxn}		
		423 K	473 K	523 K
1	Phenol**** + H* ↔ HC1-1**** + *	0.40	0.41	0.41
2	HC1-1**** + H* ↔ HC1-2a**** + *	0.85	0.85	0.85
3	HC1-1**** + H* ↔ HC1-2b**** + *	0.80	0.80	0.80
4	HC1-2a**** + H* ↔ HC1-3a**** + *	0.50	0.50	0.50
5	HC1-2a**** + H* ↔ HC1-3b**** + *	0.57	0.57	0.57
6	HC1-2a**** + H* ↔ HC1-3c**** + *	0.49	0.49	0.49
7	HC1-2a**** + H* ↔ HC1-3d**** + *	0.58	0.58	0.59
8	HC1-2b**** + H* ↔ HC1-3e**** + *	0.63	0.63	0.63
9	HC1-2b**** + H* ↔ HC1-3f**** + *	0.48	0.47	0.46
10	HC1-2b**** + H* ↔ HC1-3g**** + *	0.16	0.16	0.15
11	HC1-2b**** + H* ↔ HC1-3h**** + *	0.64	0.64	0.64
12	HC1-3a**** + H* ↔ HC1-4a**** + *	0.00	-0.01	-0.02
13	HC1-3b**** + H* ↔ HC1-4a**** + *	-0.07	-0.08	-0.08
14	HC1-3c**** + H* ↔ HC1-4b**** + *	0.01	0.01	0.00
15	HC1-3d**** + H* ↔ HC1-4b**** + *	-0.08	-0.09	-0.10
16	HC1-3e**** + H* ↔ HC1-4c**** + *	0.09	0.08	0.08
17	HC1-3f**** + H* ↔ HC1-4c**** + *	0.24	0.25	0.25
18	HC1-3g**** + H* ↔ HC1-4d**** + *	0.40	0.39	0.39
19	HC1-3h**** + H* ↔ HC1-4d**** + *	-0.08	-0.09	-0.10
20	HC1-4a**** + H* ↔ HC1-5a**** + *	0.26	0.26	0.26
21	HC1-4a**** + H* ↔ HC1-5b**** + *	0.67	0.67	0.67
22	HC1-4b**** + H* ↔ HC1-5c**** + *	0.27	0.27	0.27
23	HC1-4b**** + H* ↔ HC1-5d**** + *	0.65	0.64	0.64
24	HC1-4c**** + H* ↔ HC1-5e**** + *	0.44	0.43	0.43
25	HC1-4c**** + H* ↔ HC1-5f**** + *	0.47	0.47	0.47
26	HC1-4d**** + H* ↔ HC1-5g**** + *	0.27	0.27	0.27
27	HC1-4d**** + H* ↔ HC1-5h**** + *	0.64	0.64	0.64
28	HC1-5a**** + H* ↔ HC-6**** + *	-0.16	-0.17	-0.17
29	HC1-5b**** + H* ↔ HC-6**** + *	-0.57	-0.58	-0.59
30	HC1-5c**** + H* ↔ HC-6**** + *	-0.17	-0.18	-0.18
31	HC1-5d**** + H* ↔ HC-6**** + *	-0.55	-0.56	-0.56
32	HC1-5e**** + H* ↔ HC-6**** + *	-0.51	-0.51	-0.51
33	HC1-5f**** + H* ↔ HC-6**** + *	-0.55	-0.55	-0.55
34	HC1-5g**** + H* ↔ HC-6**** + *	-0.17	-0.18	-0.18
35	HC1-5h**** + H* ↔ HC-6**** + *	-0.55	-0.55	-0.56
36	HC-6**** + 2* ↔ KET-6**** + 2H*	-0.50	-0.49	-0.49

37	Phenol**** + H* ↔ HC2-1**** + *	0.58	0.58	0.58
38	HC2-1**** + H* ↔ HC2-2a**** + *	0.62	0.62	0.63
39	HC2-1**** + H* ↔ HC2-2b**** + *	0.78	0.78	0.78
40	HC2-2b**** + H* ↔ HC2-3a**** + *	0.47	0.47	0.48
41	HC2-2b**** + H* ↔ HC2-3b**** + *	0.46	0.46	0.47
42	HC2-2b**** + H* ↔ HC2-3c**** + *	0.57	0.57	0.57
43	HC2-2b**** + H* ↔ HC2-3d**** + *	0.50	0.50	0.50
44	HC2-3a**** + H* ↔ HC2-4a**** + *	0.09	0.09	0.09
45	HC2-3b**** + H* ↔ HC2-4a**** + *	0.10	0.10	0.10
46	HC2-3c**** + H* ↔ HC2-4b**** + *	-0.21	-0.22	-0.22
47	HC2-3d**** + H* ↔ HC2-4b**** + *	-0.14	-0.14	-0.15
48	HC2-4b**** + H* ↔ HC2-5a**** + *	0.30	0.30	0.31
49	HC2-4b**** + H* ↔ HC2-5b**** + *	0.23	0.23	0.24
50	HC2-5a**** + H* ↔ HC-6**** + *	-0.17	-0.18	-0.18
51	HC2-5b**** + H* ↔ HC-6**** + *	-0.10	-0.11	-0.11
52	Phenol**** + H* ↔ HC3-1**** + *	0.51	0.51	0.51
53	HC3-1**** + H* ↔ HC3-2a**** + *	0.72	0.72	0.72
54	HC3-1**** + H* ↔ HC3-2b**** + *	0.74	0.74	0.74
55	HC3-2a**** + H* ↔ HC3-3a**** + *	0.12	0.11	0.11
56	HC3-2a**** + H* ↔ HC3-3b**** + *	0.57	0.57	0.57
57	HC3-2a**** + H* ↔ HC3-3c**** + *	0.52	0.52	0.53
58	HC3-2a**** + H* ↔ HC3-3d**** + *	0.09	0.09	0.09
59	HC3-2b**** + H* ↔ HC3-3e**** + *	0.55	0.55	0.56
60	HC3-2b**** + H* ↔ HC3-3f**** + *	0.59	0.59	0.60
61	HC3-2b**** + H* ↔ HC3-3g**** + *	0.48	0.49	0.49
62	HC3-2b**** + H* ↔ HC3-3h**** + *	0.58	0.58	0.59
63	HC3-3a**** + H* ↔ HC3-4a**** + *	0.39	0.39	0.39
64	HC3-3b**** + H* ↔ HC3-4a**** + *	-0.06	-0.06	-0.07
65	HC3-3c**** + H* ↔ HC3-4b**** + *	0.01	0.00	-0.01
66	HC3-3d**** + H* ↔ HC3-4b**** + *	0.43	0.43	0.43
67	HC3-3e**** + H* ↔ HC3-4c**** + *	-0.07	-0.07	-0.08
68	HC3-3f**** + H* ↔ HC3-4c**** + *	-0.11	-0.11	-0.11
69	HC3-3g**** + H* ↔ HC3-4d**** + *	0.20	0.19	0.19
70	HC3-3h**** + H* ↔ HC3-4d**** + *	0.10	0.10	0.09
71	HC3-4a**** + H* ↔ HC3-5a**** + *	0.22	0.22	0.22
72	HC3-4a**** + H* ↔ HC3-5b**** + *	0.27	0.28	0.28
73	HC3-4d**** + H* ↔ HC3-5c**** + *	0.46	0.46	0.46
74	HC3-4d**** + H* ↔ HC3-5d**** + *	0.43	0.42	0.42
75	HC3-5a**** + H* ↔ HC-6**** + *	-0.11	-0.11	-0.12
76	HC3-5b**** + H* ↔ HC-6**** + *	-0.16	-0.17	-0.18
77	Phenol**** + H* ↔ HC4-1**** + *	0.71	0.71	0.71
78	HC4-1**** + H* ↔ HC4-2a**** + *	0.52	0.52	0.52
79	HC4-1**** + H* ↔ HC4-2b**** + *	0.54	0.55	0.56
80	Phenol**** + * ↔ KET-1**** + H*	-0.77	-0.76	-0.76

81	KET-1**** + H* ↔ KET-2a**** + *	0.99	0.99	0.99
82	KET-2a**** + H* ↔ KET-3a**** + *	0.62	0.62	0.62
83	KET-2a**** + H* ↔ KET-3b**** + *	0.45	0.45	0.45
84	KET-2a**** + H* ↔ KET-3c**** + *	0.31	0.31	0.31
85	KET-2a**** + H* ↔ KET-3d**** + *	0.76	0.76	0.76
86	KET-3a**** + H* ↔ KET-4a**** + *	0.51	0.51	0.51
87	KET-3b**** + H* ↔ KET-4a**** + *	0.68	0.68	0.68
88	KET-3c**** + H* ↔ KET-4b**** + *	0.32	0.32	0.32
89	KET-3d**** + H* ↔ KET-4b**** + *	-0.12	-0.13	-0.13
90	KET-4a**** + H* ↔ KET-5a**** + *	0.45	0.44	0.44
91	KET-4a**** + H* ↔ KET-5b**** + *	0.35	0.35	0.35
92	KET-4b**** + H* ↔ KET-5c**** + *	0.17	0.17	0.16
93	KET-4b**** + H* ↔ KET-5d**** + *	0.81	0.82	0.82
94	KET-5a**** + H* ↔ KET-6**** + *	-0.45	-0.45	-0.45
95	KET-5b**** + H* ↔ KET-6**** + *	-0.35	-0.36	-0.36
96	KET-5c**** + H* ↔ KET-6**** + *	0.31	0.32	0.32
97	KET-5d**** + H* ↔ KET-6**** + *	-0.33	-0.33	-0.34
98	KET-6**** + H* ↔ KET-7a**** + *	0.61	0.60	0.60
99	KET-6**** + H* ↔ KET-7b**** + *	0.36	0.36	0.36
100	KET-7a**** + H* ↔ HC-6**** + *	-0.11	-0.11	-0.12
101	KET-7b**** + H* ↔ HC-6**** + *	0.13	0.13	0.12
102	KET-1**** + H* ↔ KET-2b**** + *	0.94	0.94	0.94
103	KET-2b**** + H* ↔ KET-3e**** + *	0.28	0.28	0.28
104	KET-2b**** + H* ↔ KET-3f**** + *	0.82	0.82	0.82
105	KET-2b**** + H* ↔ KET-3g**** + *	0.27	0.27	0.27
106	KET-2b**** + H* ↔ KET-3h**** + *	0.82	0.82	0.82
107	KET-3e**** + H* ↔ KET-4c**** + *	0.47	0.47	0.46
108	KET-3f**** + H* ↔ KET-4c**** + *	-0.06	-0.07	-0.08
109	KET-3g**** + H* ↔ KET-4d**** + *	0.42	0.42	0.42
110	KET-3h**** + H* ↔ KET-4d**** + *	-0.13	-0.13	-0.14
111	KET-4c**** + H* ↔ KET-5e**** + *	0.10	0.09	0.09
112	KET-4c**** + H* ↔ KET-5f**** + *	0.77	0.77	0.78
113	KET-5e**** + H* ↔ KET-6**** + *	0.33	0.33	0.34
114	KET-5f**** + H* ↔ KET-6**** + *	-0.34	-0.35	-0.35



HC1-1



HC1-2a

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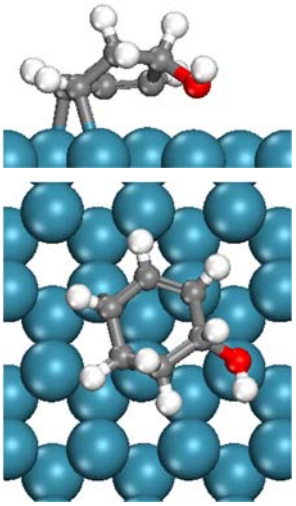

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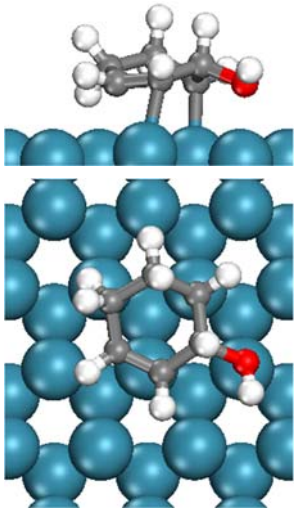

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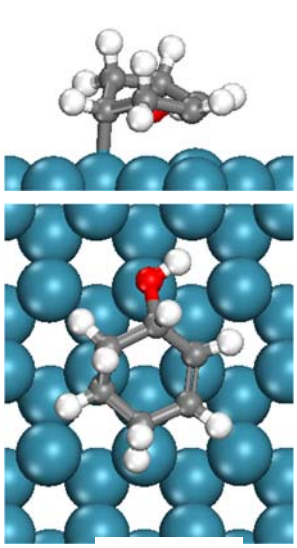

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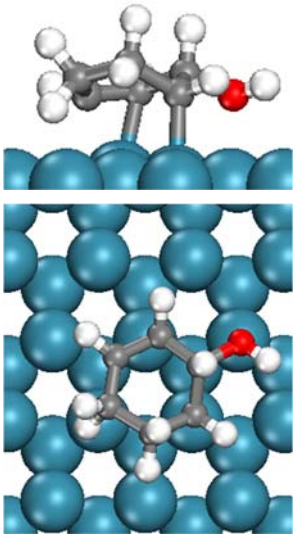

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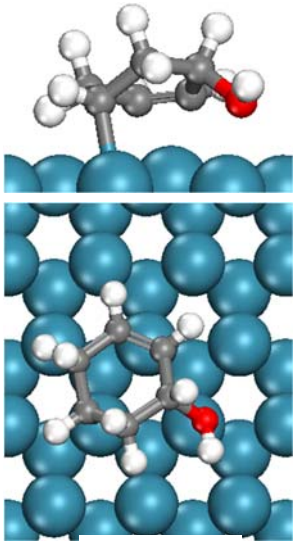

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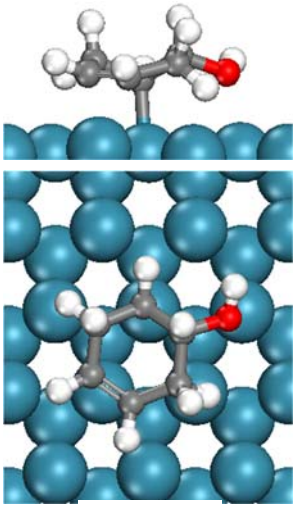

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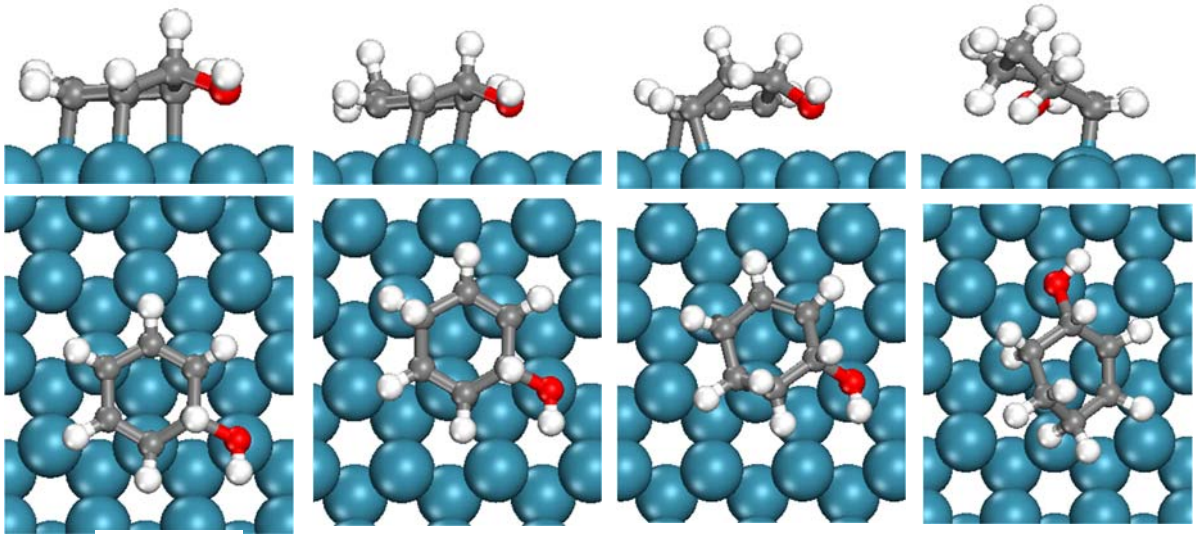
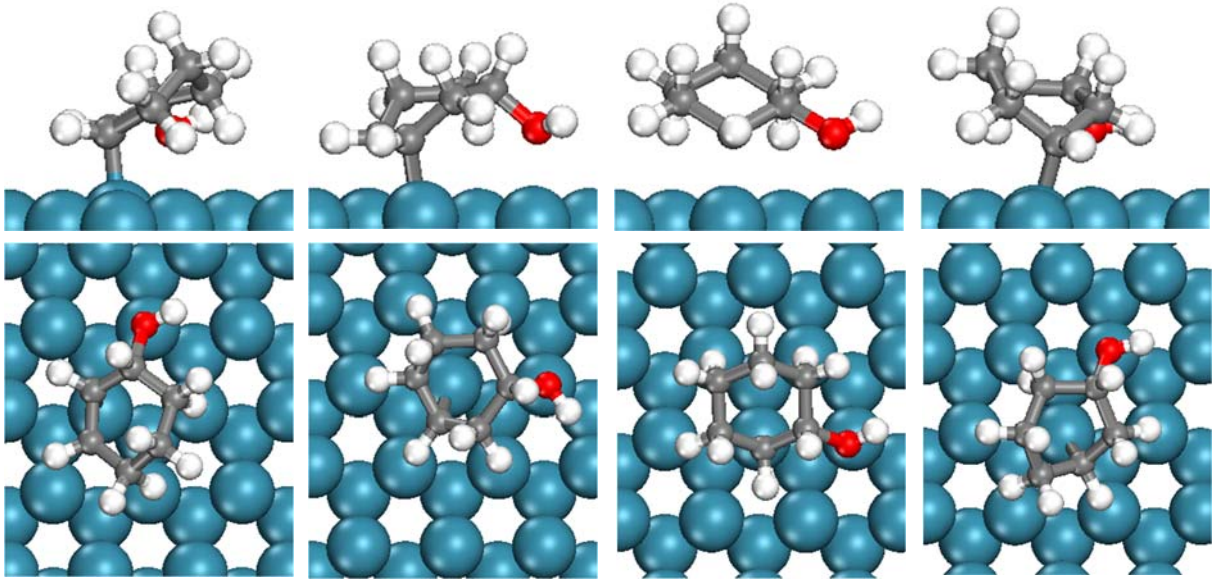


HC1-3f HC1-3g HC1-3h HC1-4a



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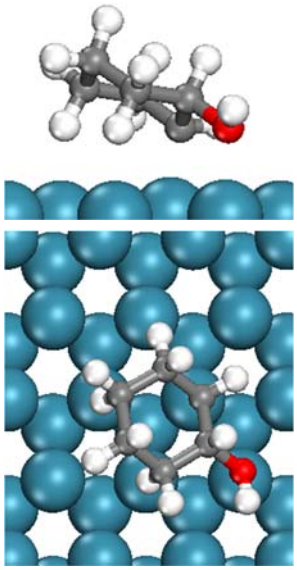
HC1-4c = HC2-4a

HC1-5a

HC1-5b



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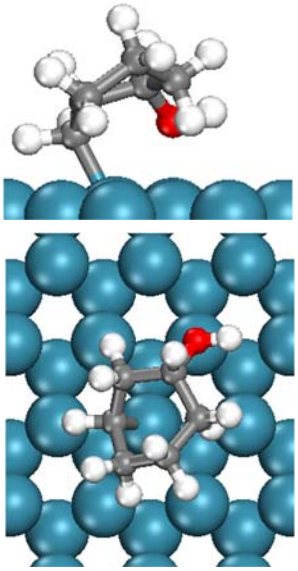

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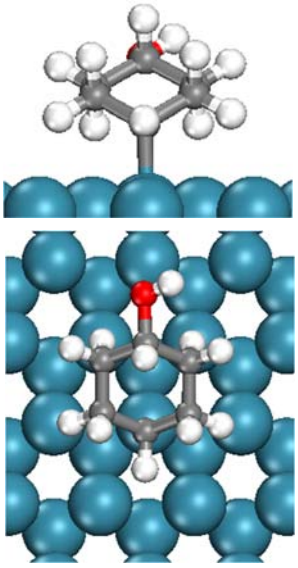

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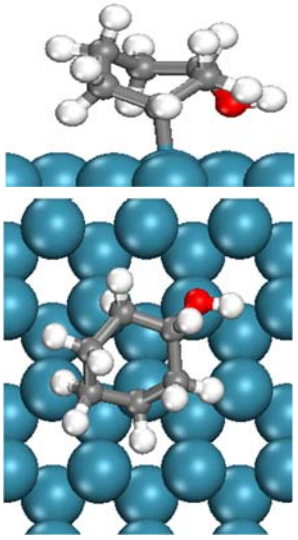

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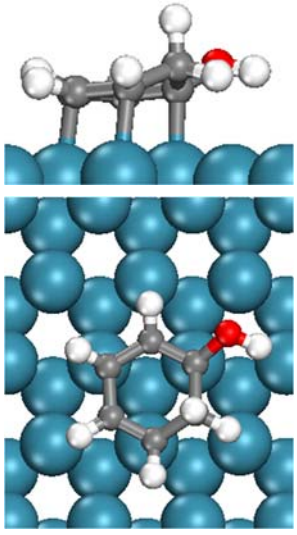

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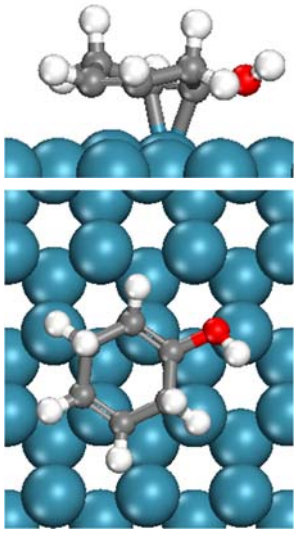

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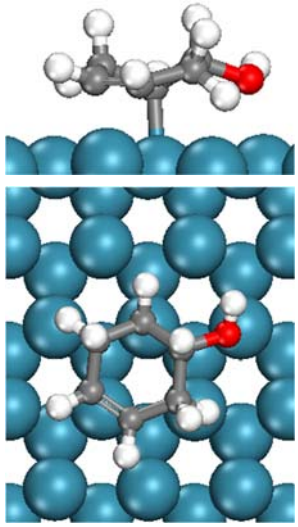

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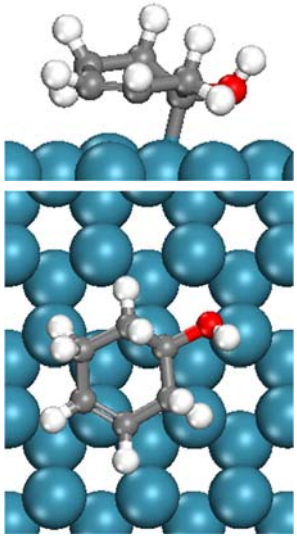
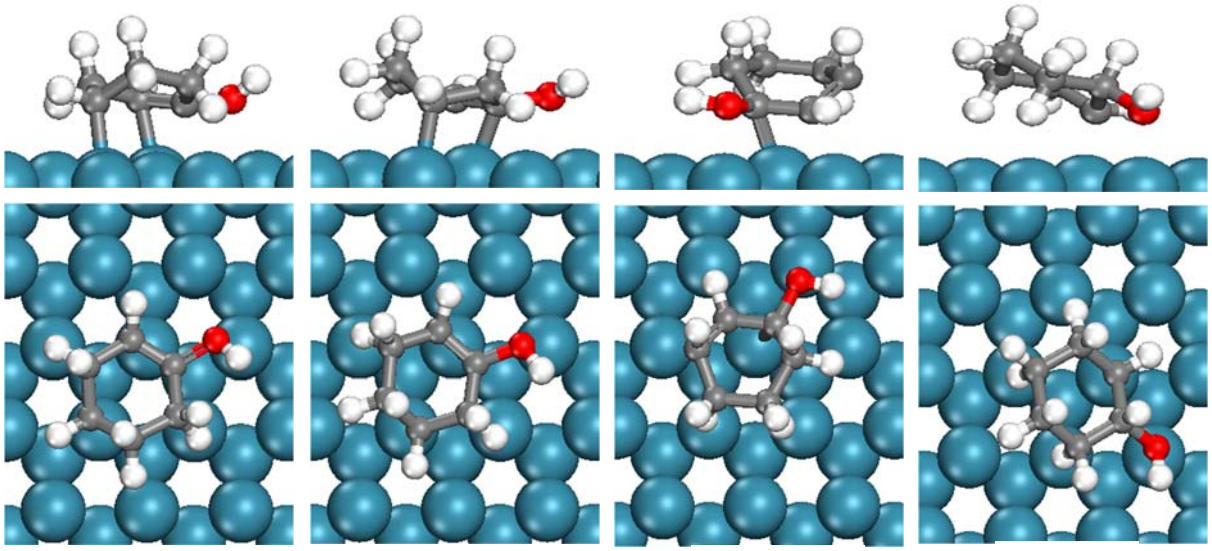
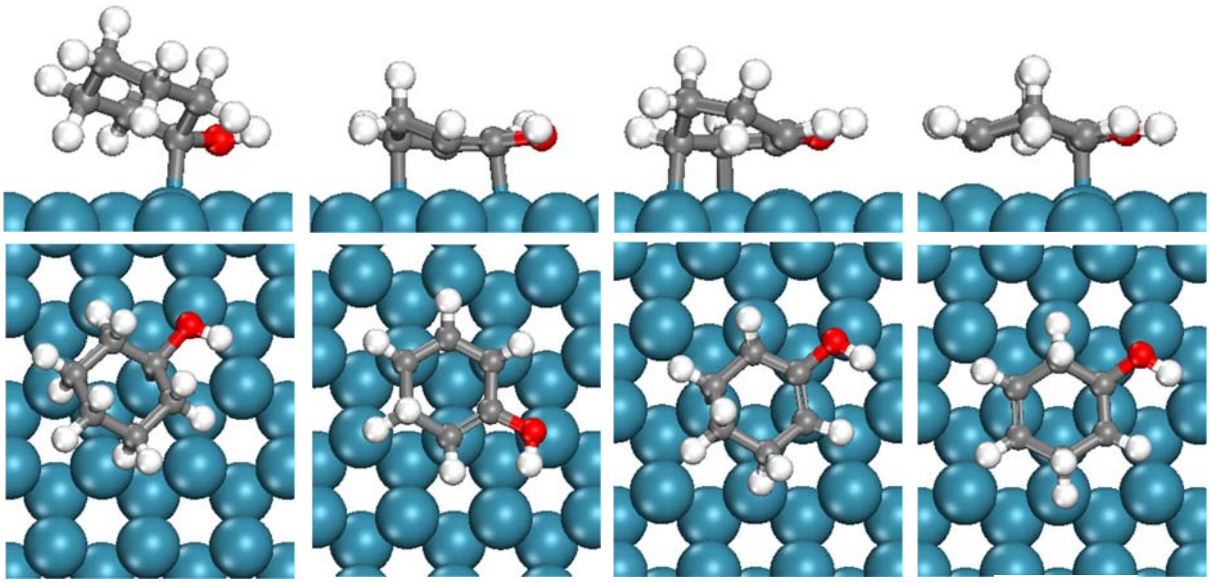


HC2-3b

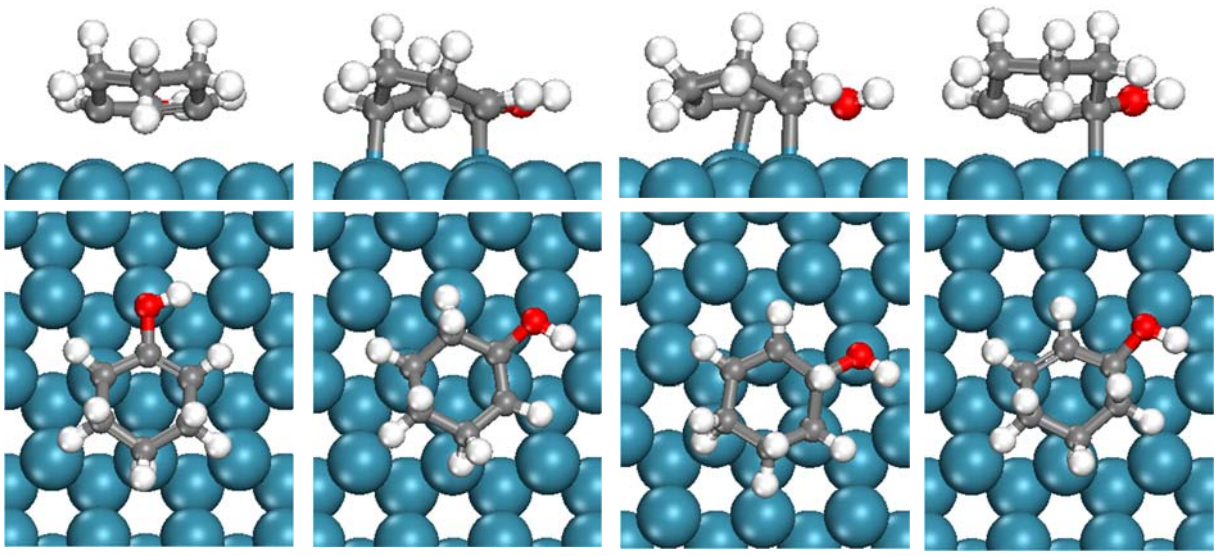


HC2-3c HC2-3d HC2-4b HC2-5a

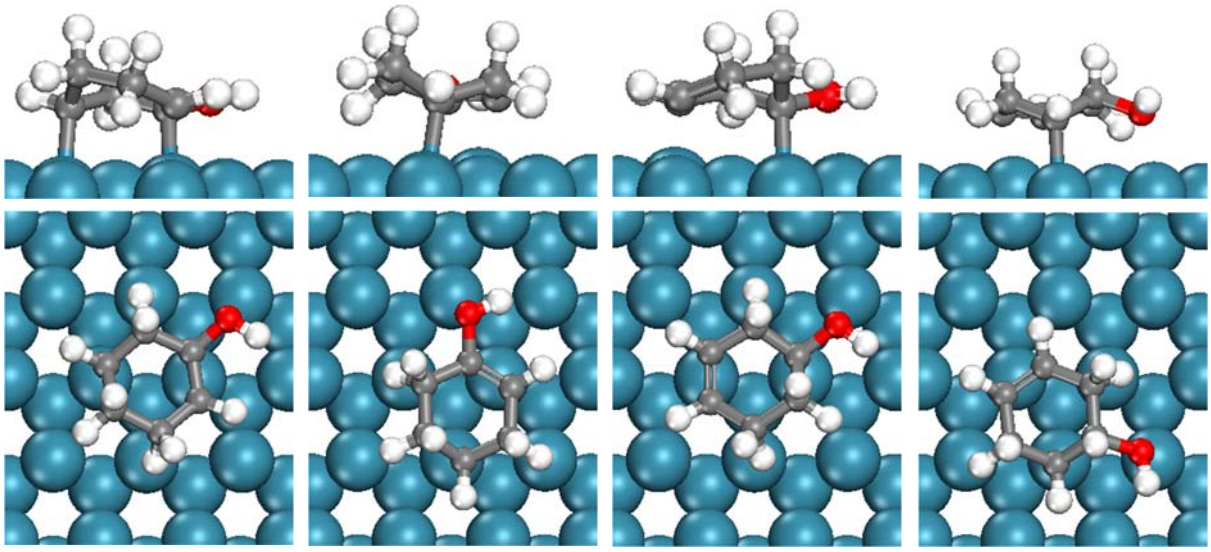


HC2-5b HC3-1 HC3-2a HC3-2b

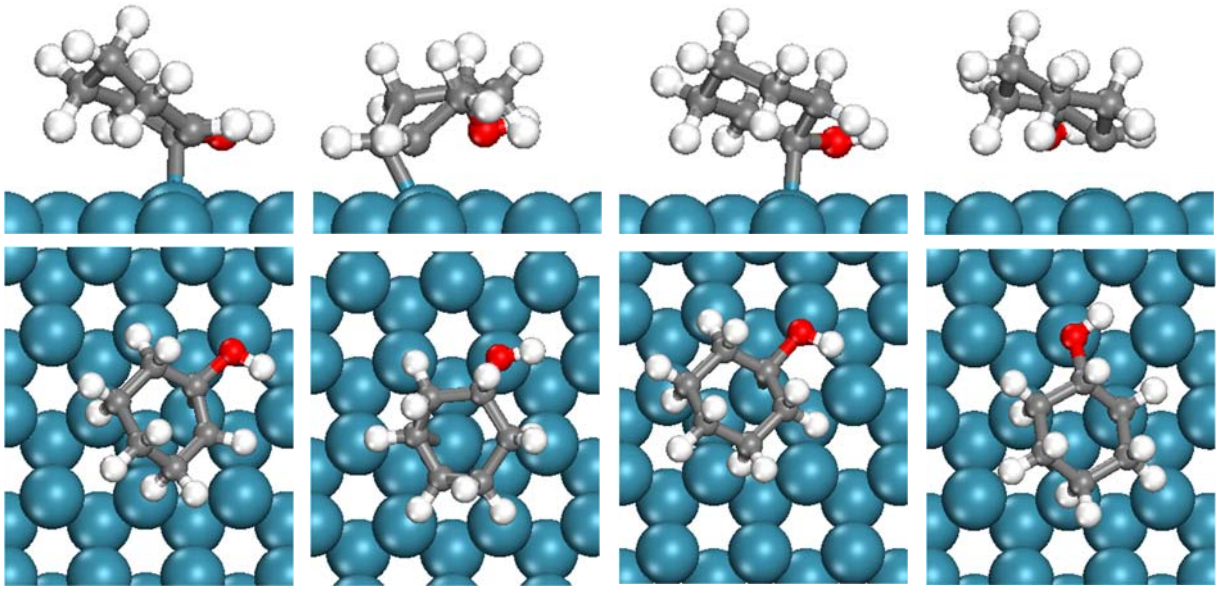
= HC 4-2a



HC3-3a HC3-3b HC3-3c HC3-3d



HC3-3e HC3-3f HC3-3g HC3-3h



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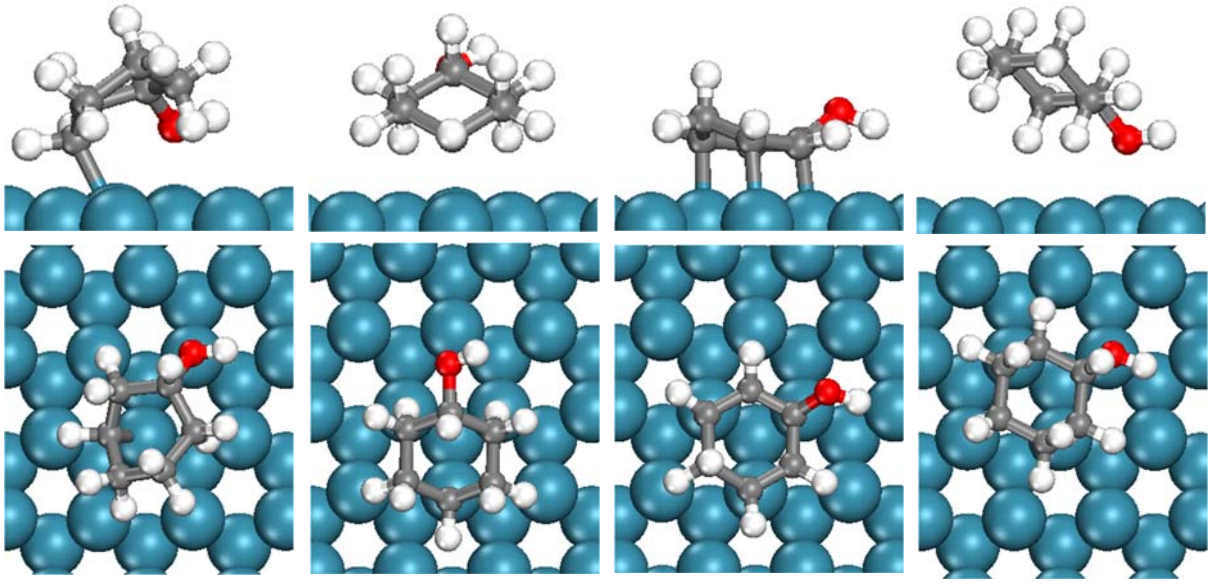
HC3-4d

HC3-5a

HC3-5b



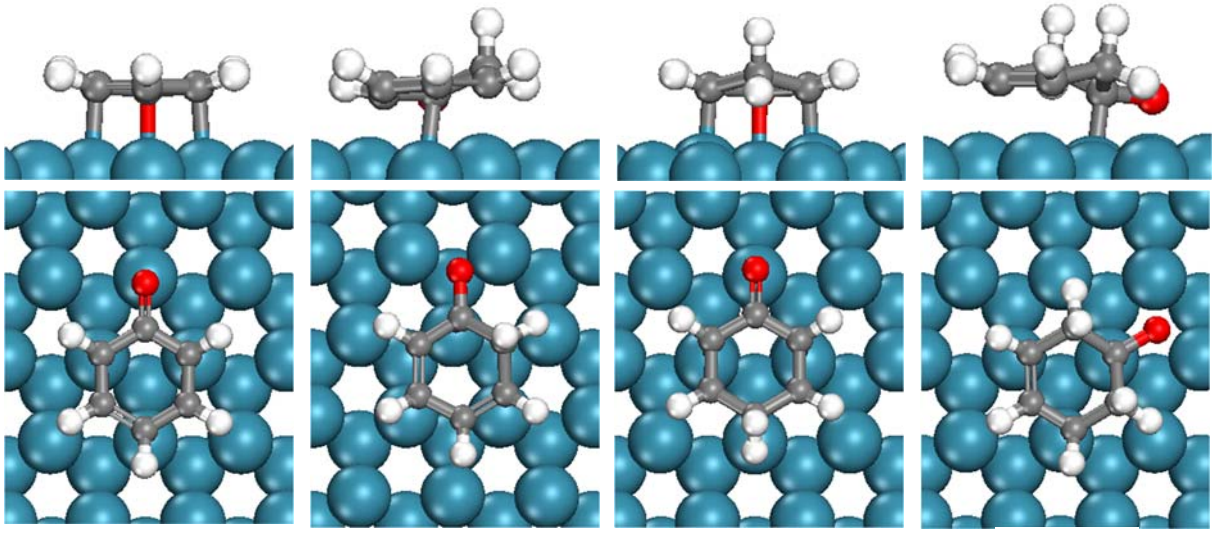
HC3-5c

HC3-5d

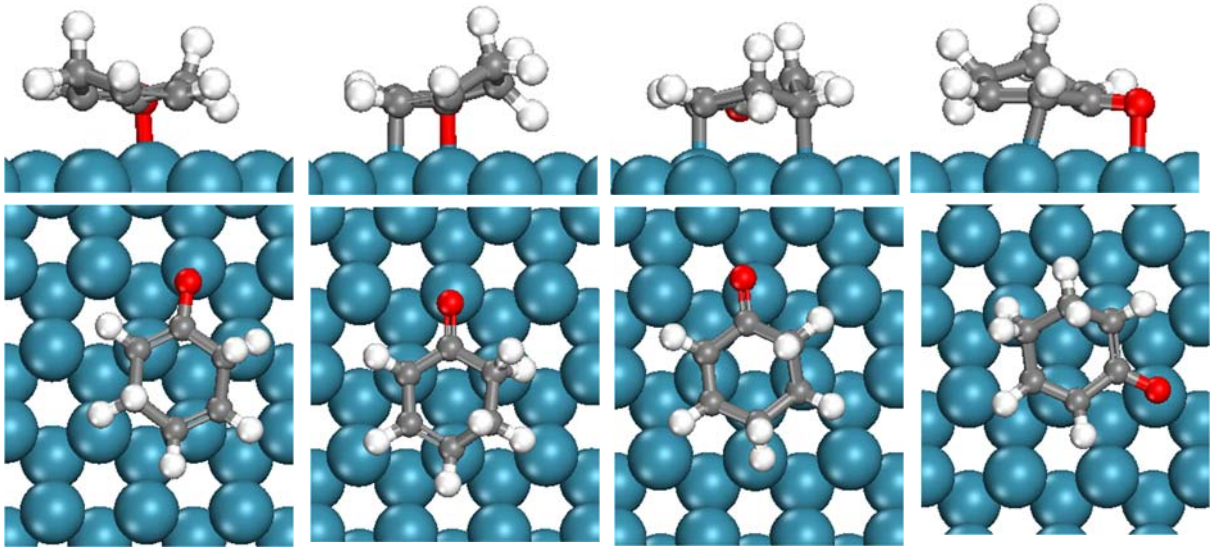
HC4-1

HC-6

Cyclohexanol



KET-1 KET-2a KET-2b KET-3a



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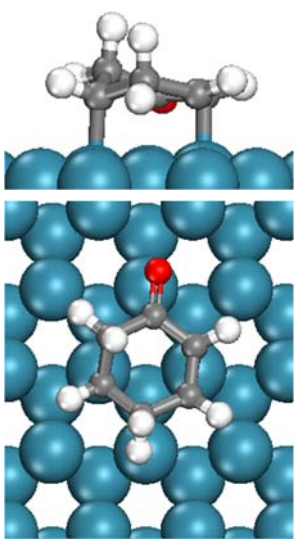

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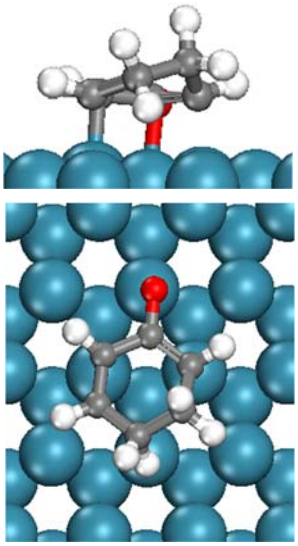

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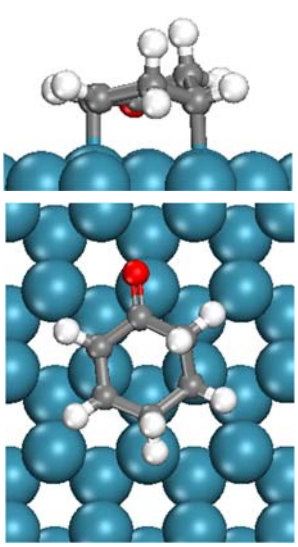

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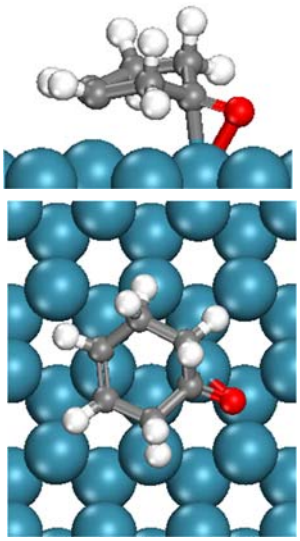

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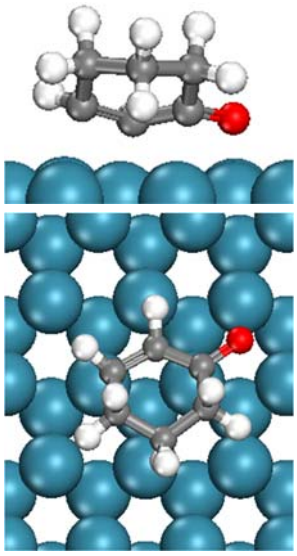
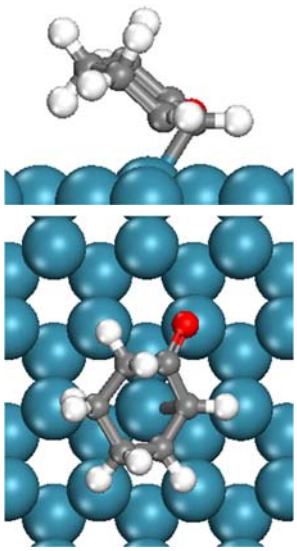


KET-4b

= KET-4d



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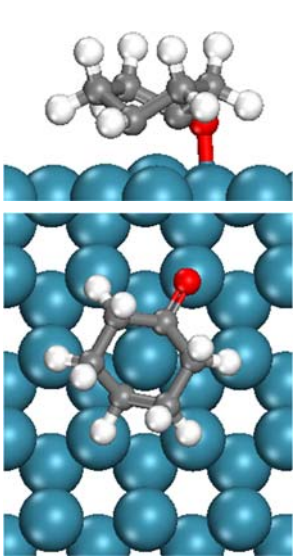

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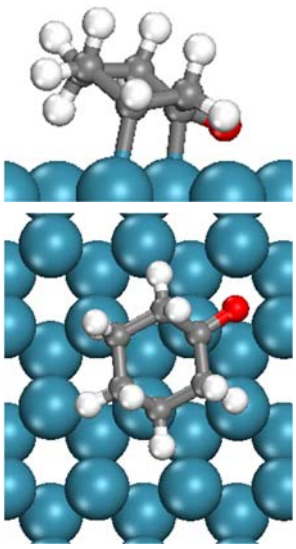

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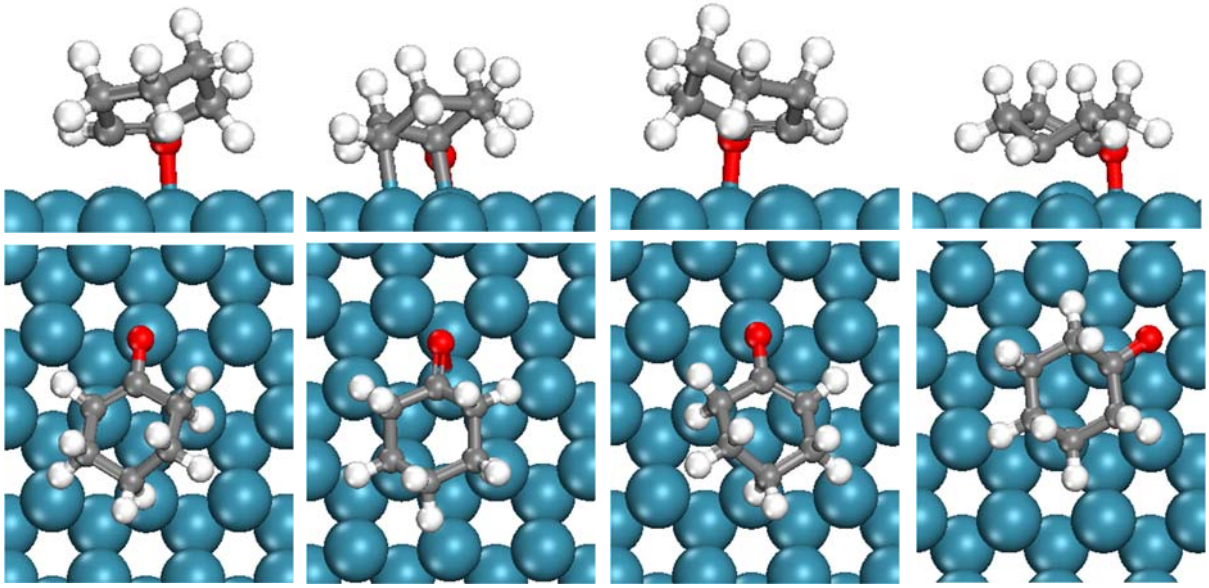
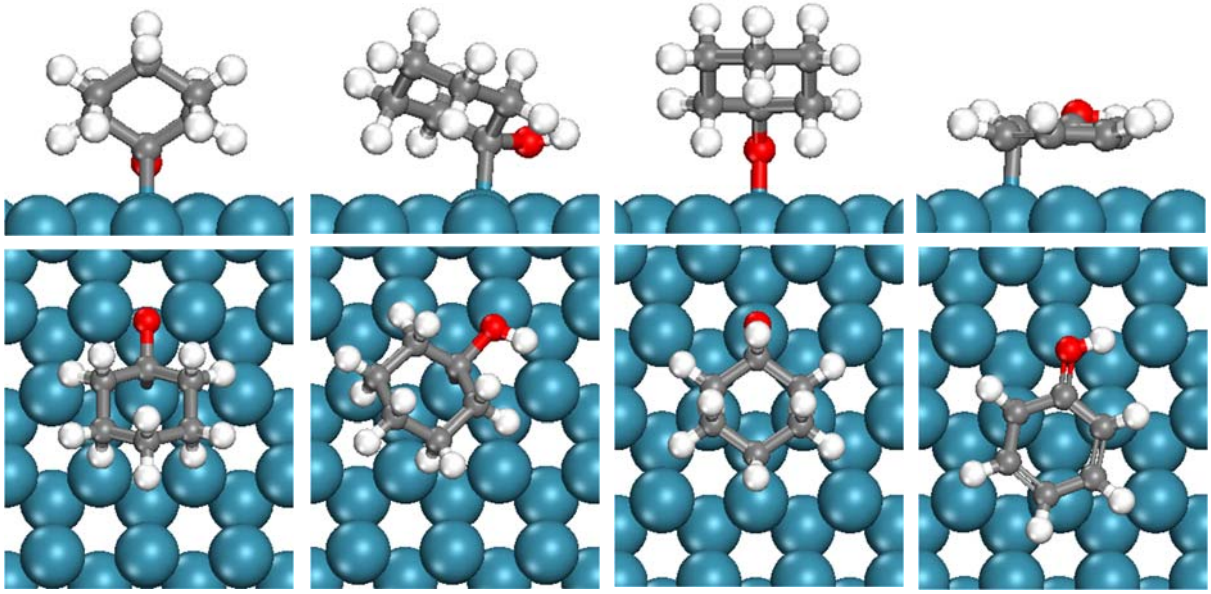


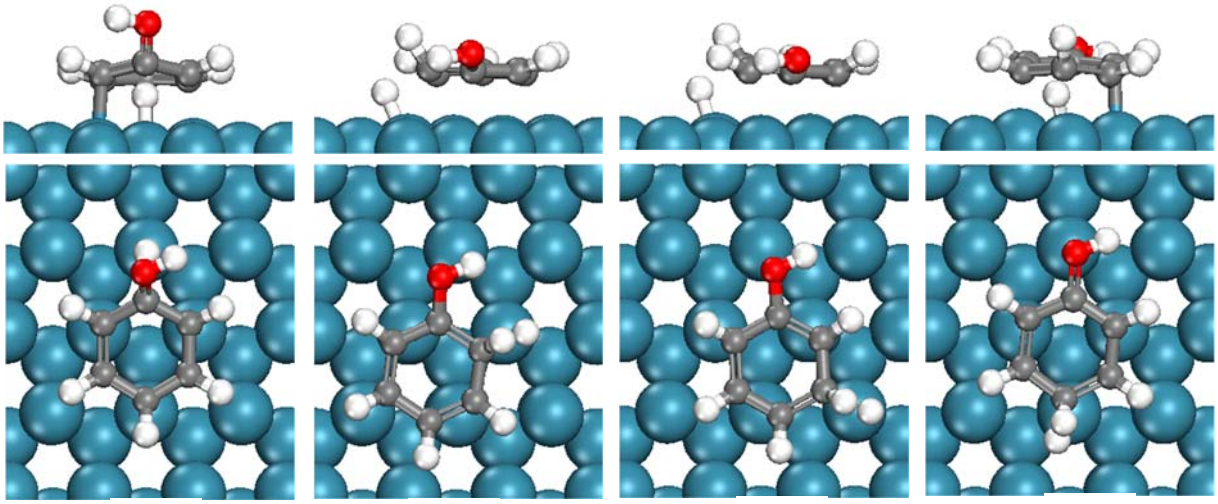
KET-5c KET-5d KET-5e KET-5f



KET-6 KET-7a KET-7b Phenol

Cyclohexanone

Figure S1: Preferred adsorption geometries of the various intermediates involved in the phenol HDO reaction network. For the purpose of clarity, side (upper panel) and top (lower panel) views are displayed here.



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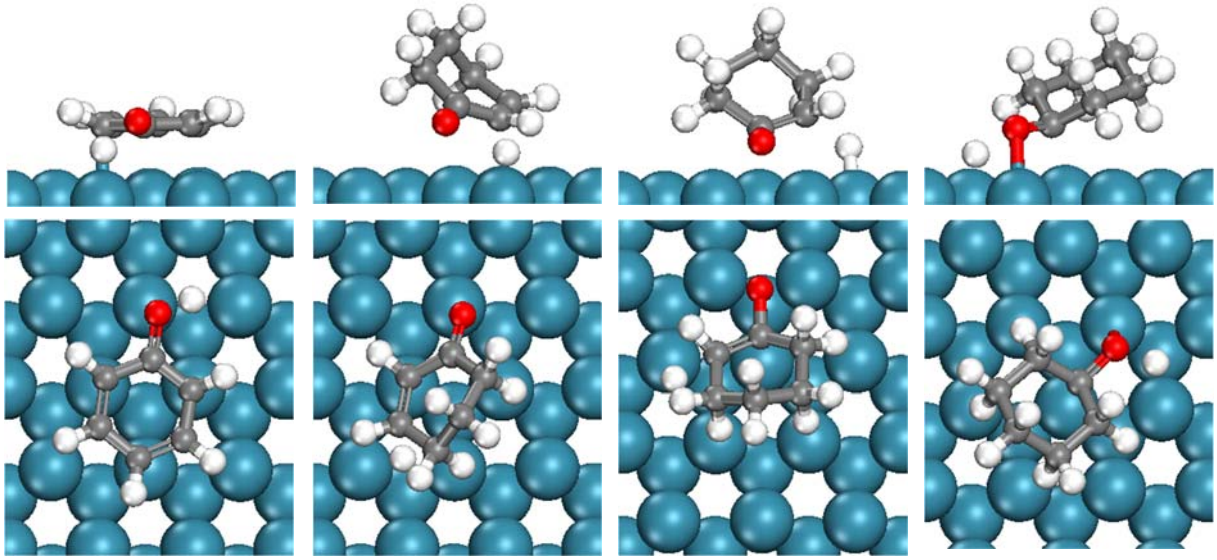

80 92 96 98

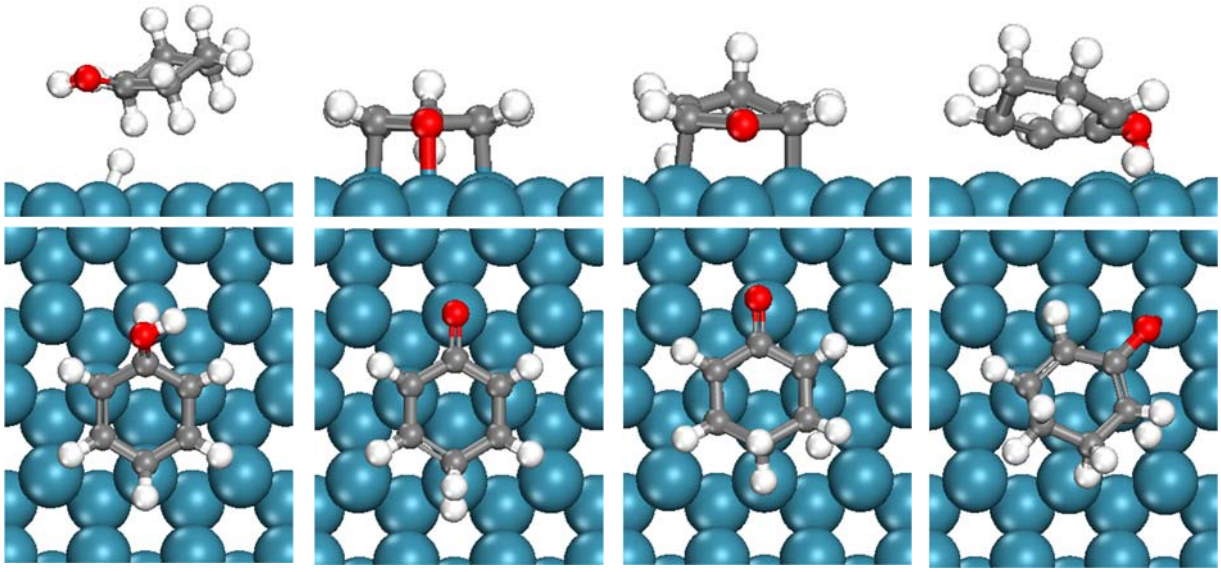

Figure S2: Side (upper panel) and top (lower panel) views of the transition state structures investigated for the phenol HDO reaction network.