Electronic Supporting information

Interface-tuned Selective Reductive Coupling of Nitroarenes to Aromatic Azo and Azoxy: a First-principles-based Microkinetics Study

Lidong Zhang [a], Zheng-Jiang Shao, Xiao-Ming Cao [a,*], and P. Hu [a,b,*]

[a] *Key Laboratory for Advanced Materials, Center for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P. R. China*

[b] *School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast, BT9 5AG, U. K.*

[*] Corresponding Authors:

E-mail address: xmcao@ecust.edu.cn (Xiao-Ming Cao) and p.hu@qub.ac.uk (P. Hu)

Computational details:

Modeling neutral conditions

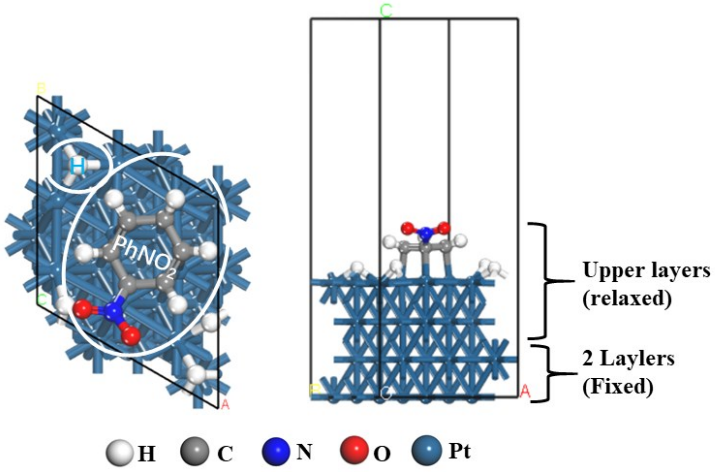


Fig. S1 The model of nitrobenzene hydrogenation under neutral conditions.

Modeling KOH/Pt(111) interface

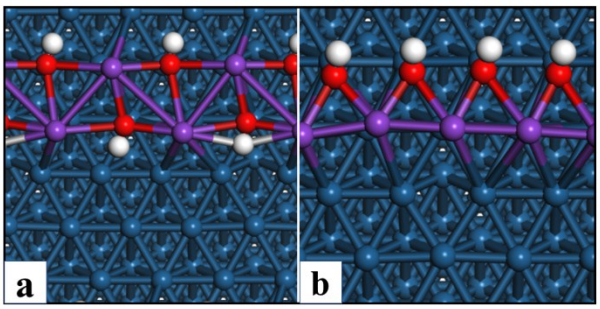
The most stable KOH/Pt(111) interface was taken as the model for the subsequent reaction simulation. Firstly, we tested the surface energies of a series of facets to identify the most stable exposed KOH facet. The calculated results were summarized in Table S1. The most stable (001) crystal plane was therefore chosen as the exposed surface.

Table S1 The surface energy (γ) of KOH crystal plane

hkl	γ (J/m^2)
(001)	0.50
(100)	3.56
$(10\bar{1})$	1.21
(011)	1.38
(110)	0.75
$(11\bar{1})$	0.72

Since different configurations of Pt/KOH interface would stem from the different

cutting orientations of KOH(001) on Pt(111). The adsorption energies per unit area E_{ad} (J/m^2) of KOH(001) on Pt(111) for different configurations were further tested to evaluate the most stable configuration. The tested configurations and the calculated E_{ad} are illustrated in Figure R1 and the calculated results are listed in Table R3. The optimal configuration of (a) with the strongest adsorption energy per unit area was finally adopted as the model for the subsequent reaction simulation.



E_{ad} = -2.52 J/m^2 **E_{ad} = -1.14 J/m^2**

Figure S2 The configurations (a) and (b) of KOH(001) on Pt(111) surface and the corresponding adsorption energy per unit area E_{ad} (J/m^2) of KOH(001) plane on the Pt(111) surface

Microkinetic data based on DFT calculation under neutral conditions

Table S1. The backward free energy of activation (G_a) and free energy of reaction (ΔG) of each elementary step in the $PhNO_2$ hydrogenation under the neutral reaction condition.

Step	Reactions	G_a (eV)	ΔG (eV)
1	$PhNO_2$*+H* → PhNOOH* (1a → TS(1a/1b) → 1b)	0.28	0.23
2	$PhNO_2$* → PhNO* + O* (1a → TS(1a/1l) → 1l)	0.68	-1.53
3	PhNOOH*+H* → $PhN(OH)_2$* (1b → TS(1b/1c) → 1c)	0.20	0.09
4	PhNOOH* → PhNO* + OH* 1b → TS(1b/1d) → 1d	0.62	-0.09
5	PhNO* → PhN* + O* (1f → TS(1f/1m) → 1m)	1.40	-0.57
6	PhN*+H* → PhNH* (1n → TS(1n/1j) → 1j)	1.47	0.93
7	$PhN(OH)_2$* →PhNOH* + OH* (1c → TS(1c/1e) → 1e)	0.73	0.02
8	H* + OH*→ H_2O(g) (PhNO) (1d → TS(1d/1f) → 1f)	1.09	0.92
9	PhNO* + H* → PhNOH* (1f → TS(1f/1g) → 1g)	0.47	0.35
10	PhNO* + H* → PhNHO* (1f → TS(1f/1o) → 1o)	0.89	0.44
11	H* + OH* → H_2O(g) (PhNOH) (1e → TS(1e/1g) → 1g)	1.08	0.88
12	PhNOH* + H* → PhNHOH* (1g → TS(1g/1h) → 1h)	0.98	0.63
13	PhNHO* + H* → PhNHOH* (1o → TS(1o/1h) → 1h)	0.57	0.54
14	PhNHOH* → PhNH* + OH* (1h → TS(1h/1i) → 1i)	1.19	0.33
15	H* + OH* → H_2O(g) (PhNH) (1i → TS(1i/1j) → 1j)	1.24	1.10
16	PhNH* + H* → $PhNH_2$* (1j → TS(1j/1k) → 1k)	0.87	0.79
17	PhNOH* → PhN* + OH*	0.28	-1.64

	(1g → TS(1g/1l) → 1l)		
18	PhNO*+PhNO*→PhN(O)N(O)Ph*	0.92	-0.26
19	PhN(O)N(O)Ph*+H*→PhN(OH)N(O)Ph*	0.15	-0.11
20	PhN(OH)N(O)Ph*→PhNN(O)Ph*+OH*	2.49	1.43
21	PhNOH* +PhNOH* → PhN(OH)N(OH)Ph*	0.76	-0.57
22	PhN(OH)N(OH)Ph*→PhN(OH)NPh*+OH*	1.33	0.63
23	PhN(OH)NPh* + * →PhN(O)NPh*+H*	0.12	-0.01
24	PhN(OH)NPh* + * →PhNNPh*+OH*	1.07	0.17
24	PhNOH* + PhNO* → PhN(OH)N(O)Ph*	0.90	-0.78

Table S2. The forward rate r_+, reverse rate r_-, net rate r_i, imaginary vibrational frequency value of TS (f/i), reversibility Z_i and sensitive degree of rate control $X_{RC,i}$* of each step during $PhNO_2$ hydrogenation over Pt(111) under the neutral conditions.

	Step	r_+ (s^{-1})	r_- (s^{-1})	r_i (s^{-1})	Z_i	$X_{RC,i}$		f/i(cm^{-1})
						direct	condensation	
R1	$PhNO_2(g) + * \rightleftarrows PhNO_2*$	2.49E-03	6.64E-19	2.49E-03	2.67E-16	0.00	0.02	–
R2	$H_2(g) + 2* \rightleftarrows 2H*$	1.25E+04	1.25E+04	7.47E-03	1.00E+00	0.00	0.00	–
R3	$PhNO_2* + H* \rightleftarrows PhNOOH* + *$	2.64E-03	1.47E-04	2.49E-03	5.58E-02	0.00	0.00	280.44
R4	$PhNOOH* + H* \rightleftarrows PhN(OH)_2* + *$	2.47E+00	2.47E+00	2.49E-03	9.99E-01	0.00	0.00	166.78
R5	$PhNOOH* + * \rightleftarrows PhNO* + OH*$	2.07E-09	4.10E-23	2.07E-09	1.98E-14	0.00	0.00	168.6
R6	$PhN(OH)_2* + * \rightleftarrows PhNOH* + OH*$	2.49E-03	1.26E-17	2.49E-03	5.07E-15	0.00	0.00	322.8
R7	$H* + OH* \rightleftarrows H_2O* + *$	4.98E-03	1.44E-17	4.98E-03	2.88E-15	0.00	0.00	287.26
R8	$PhNO* + H* \rightleftarrows PhNOH* + *$	4.18E-08	3.98E-08	2.07E-09	9.51E-01	0.00	0.00	245.57
R9	$PhNO* + H* \rightleftarrows PhNHO* + *$	4.24E-14	1.50E-13	-1.08E-13	3.54E+00	0.00	-	531.31
R10	$PhNOH* + H* \rightleftarrows PhNHOH* + *$	3.44E+00	3.43E+00	2.49E-03	9.99E-01	0.00	-	461.36
R11	$PhNHO* + H* \rightleftarrows PhNHOH* + *$	4.72E+04	4.72E+04	-1.08E-13	1.00E+00	0.00	-	153.64
R12	$PhNHOH* + * \rightleftarrows PhNH* + OH*$	2.49E-03	4.82E-28	2.49E-03	1.94E-25	1.00	-	181.21
R13	$PhNH* + H* \rightleftarrows PhNH_2* + *$	2.49E-03	6.15E-11	2.49E-03	2.47E-08	0.00	-	144.42
R14	$H_2O* \rightleftarrows H_2O + *$	4.99E-03	9.48E-06	4.98E-03	1.90E-03	0.00	-	–
R15	$PhNH_2* \rightleftarrows PhNH_2 + *$	5.37E+01	5.37E+01	2.49E-03	1.00E+00	0.00	-	–
R16	$PhNO* + PhNO* \rightleftarrows PhN(O)N(O)Ph* + *$	1.60E-35	1.09E-35	5.01E-36	6.86E-01	-	0.00	198.99
R17	$PhN(O)N(O)Ph* + H* \rightleftarrows PhN(O)N(OH)Ph* + *$	4.86E-23	4.86E-23	5.01E-36	1.00E+00	-	0.00	397.3
R18	$PhN(O)N(OH)Ph* + * \rightleftarrows PhN(O)NPh* + OH*$	5.01E-36	2.25E-63	5.01E-36	4.49E-28	-	0.00	462.42
R19	$PhNOH* + PhNOH* \rightleftarrows PhN(OH)N(OH)Ph* + *$	5.48E-28	2.50E-36	5.48E-28	4.56E-09	-	0.96	308.29
R20	$PhN(OH)N(OH)Ph* + * \rightleftarrows PhN(OH)NPh + OH*$	5.48E-28	1.17E-42	5.48E-28	2.14E-15	-	0.02	188.34
R21	$PhN(OH)NPh* + * \rightleftarrows PhN(O)NPh* + H*$	3.81E-17	3.81E-17	-4.93E-36	1.00E+00		0.00	311.67
R22	$PhN(OH)NPh* + * \rightleftarrows PhNNPh* + OH*$	2.02E-27	1.47E-27	5.48E-28	7.29E-01	-	0.00	328.44
R23	$PhNO* + PhNOH* \rightleftarrows PhN(O)N(OH)Ph* + *$	3.03E-41	3.15E-41	-1.24E-42	1.04E+00	-	0.00	282.79
R24	$PhN(O)NPh* \rightleftarrows PhN(O)NPh + *$	7.86E-38	0.00E+00	7.86E-38	0.00E+00	-	0.00	–
R25	$PhNNPh* \rightleftarrows PhNNPh + *$	5.48E-28	0.00E+00	5.48E-28	0.00E+00	-	0.00	–
R26	$PhNHOH* \rightleftarrows PhNHOH + *$	1.22E-23	0.00E+00	1.22E-23	0.00E+00	0.00	-	–
R27	$PhNO* \rightleftarrows PhNO + *$	9.07E-48	0.00E+00	9.07E-48	0.00E+00	0.00	-	–

* The microkinetic simulation of the reaction rate for each step and the coverage of each intermediate were based on the whole reaction network. However, to understand the importance

of each step for either direct route or condensation route, $X_{RC,i}$* were calculated separately at direct and condensation routes without considering the interaction between two routes throughout the work.

Table S3. The coverage ($\theta(j)$) and the degree of thermodynamic rate control ($X_{TRC,\ j}$) of major intermediates *j* on Pt(111) under the neutral condition.

Species	$\theta_{(j)}$	$X_{TRC,j}$
H*	3.65E-01	-0.45
$PhNO_2$*	1.09E-13	0.00
PhNOOH*	5.33E-12	0.00
$PhN(OH)_2$*	8.89E-05	0.00
PhNO*	2.41E-19	0.00
OH*	4.94E-13	0.00
H_2O*	1.68E-11	0.00
PhNOH*	1.42E-09	0.00
PhNHO*	1.41E-07	0.00
PhNHOH*	6.34E-01	-0.78
PhNH*	9.22E-14	0.00
$PhNH_2$*	3.01E-06	0.00
PhN(OH)N(OH)Ph*	1.45E-32	0.00
PhN(OH)NPh*	5.76E-49	0.00
PhN(O)N(OH)Ph*	9.57E-39	0.00
PhN(O)N(O)Ph*	9.32E-43	0.00
PhN(O)NPh*	1.52E-56	0.00
PhNNPh*	7.88E-58	0.00
*	4.18E-04	0.00

Microkinetic data based on DFT calculation at KOH/Pt(111) interface

Table S4. The backward free energy of activation (G_a) and free energy of reaction (ΔG) of each elementary step in $PhNO_2$ hydrogenation under the alkaline conditions.

Step	Reactions	G_a (eV)	ΔG (eV)
1	$PhNO_2$* → PhNO* + O* (2a → TS(2a/2k) → 2k)	1.23	0.29
2	$PhNO_2$*+H* → PhNOOH* (2a → TS(2a/2b) → 2b)	0.23	-0.13
3	PhNOOH*→PhNO*+OH* (2b → TS(2b/2c) → 2c)	1.10	1.06
4	PhNO*→PhN*+O* (2c → TS(2c/2l) → 2l)	0.59	-0.30
5	PhN*+H*→PhNH* (2g → TS(2g/2i) → 2i)	0.99	-0.28
6	PhNO*+H*→PhNOH* (2c → TS(2c/2e) → 2e)	0.34	-0.37
7	PhNO*+H*→PhNHO* (2c → TS(2c/2d) → 2d)	1.11	0.05
8	PhNOH*+H*→PhNHOH* (2e → TS(2e/2f) → 2f)	1.35	0.36
9	PhNHO*+H*→PhNHOH* (2d → TS(2d/2f) → 2f)	0.67	0.08
10	PhNHOH*→PhNH*+OH* (2f → TS(2f/2h) → 2h)	1.71	0.99
11	PhNH*+H*→$PhNH_2$* (2i → TS(2i/2j) → 2j)	1.47	0.55
12	PhNOH* → PhN* + OH* (2e → TS(2e/2g) → 2g)	1.49	1.24
13	PhNHO* → PhNH* + O* (2d → TS(2d/2m) → 2m)	0.56	-0.12
14	O* + H* → OH*	1.63	1.08
15	H* + OH*→ H_2O	0.89	0.76
16	PhNO*+PhNOH*→PhN(O)N(OH)Ph*	0.44	-0.79
17	PhNO*+PhN*→PhNN(O)Ph*	1.12	0.38
18	PhNO*+PhNO* →PhN(O)N(O)Ph*	0.06	-1.36
19	PhNOH*+PhNOH* →PhN(OH)N(OH)Ph*	0.74	0.17
20	PhNOH*+PhN* →PhN(OH)NPh*	1.17	0.38

21	PhN*+PhN*→PhNNPh*	1.57	-0.04
22	PhN(OH)N(OH)Ph*+*→PhN(OH)NPh*+OH*	1.49	0.83
23	PhN(O)NPh*+H*→PhN(OH)NPh*	0.62	-0.13
24	PhN(OH)NPh*→PhNNPh*+OH*	1.52	1.14
25	PhN(O)NPh*→PhNNPh*+O*	1.07	0.06

Table S5. The forward rate r_+, reverse rate r_-, net rate r_i, imaginary vibrational frequency value of TS (f/i), reversibility Z_i and sensitive degree of rate control $X_{RC,i}$* of each step for $PhNO_2$ hydrogenation at KOH/Pt(111) interface.

	Step	r_+ (s^{-1})	r_- (s^{-1})	r_i (s^{-1})	Z_i	$X_{RC,i}$		f/i(cm^{-1})
						direct	condensation	
R1	$PhNO_2(g) + * \rightleftarrows PhNO_2*$	2.78E-03	3.93E-16	2.78E-03	1.41E-13	0.00	0.00	–
R2	$H_2(g) + 2* \rightleftarrows 2H*$	1.31E-01	1.27E-01	4.51E-03	9.66E-01	0.00	0.00	–
R3	$PhNO_2* + H* \rightleftarrows PhNOOH* + *$	1.05E-06	2.78E-03	2.78E-03	2.66E+03	0.00	0.00	685.08
R4	$PhNOOH* + * \rightleftarrows PhNO* + OH*$	2.78E-03	1.76E-19	2.78E-03	6.33E-17	0.00	0.00	237.84
R5	$PhNO_2* + * \rightleftarrows PhNO* + O*$	2.30E-07	2.67E-13	2.30E-07	1.16E-06	0.00	0.00	434.28
R6	$H* + OH* \rightleftarrows H_2O* + *$	4.51E-03	2.60E-14	4.51E-03	5.77E-12	0.00	0.00	333.63
R7	$PhNO* + * \rightleftarrows PhN* + O*$	1.19E-10	9.45E-08	-9.44E-08	7.96E+02	0.00	0.00	370.77
R8	$PhNO* + H* \rightleftarrows PhNOH* + *$	1.43E-03	3.75E-05	1.39E-03	2.62E-02	0.00	0.00	999.21
R9	$PhNO* + H* \rightleftarrows PhNHO* + *$	1.45E-08	4.12E-18	1.45E-08	2.85E-10	0.00	0.00	889.9
R10	$PhNOH* + H* \rightleftarrows PhNHOH* + *$	4.65E-10	3.53E-15	4.65E-10	7.60E-06	0.00	-	607.77
R11	$PhNHO* + H* \rightleftarrows PhNHOH* + *$	6.84E-07	6.69E-07	1.45E-08	9.79E-01	0.00	-	424.85
R12	$PhNHOH* + * \rightleftarrows PhNH* + OH*$	1.50E-08	1.95E-29	1.50E-08	1.30E-21	0.00	-	453.42
R13	$PhNOH* + * \rightleftarrows PhN* + OH*$	1.39E-03	1.71E-23	1.39E-03	1.23E-20	0.00	0.00	298.51
R14	$PhN* + H* \rightleftarrows PhNH* + *$	7.22E-08	1.80E-14	7.22E-08	2.50E-07	1.00	-	698.97
R15	$PhNH* + H* \rightleftarrows PhNH_2* + *$	8.71E-08	2.99E-28	8.71E-08	3.43E-21	0.00	-	949.42
R16	$H_2O* \rightleftarrows H_2O + *$	5.51E+01	5.50E+01	4.51E-03	1.00E+00	0.00	0.00	–
R17	$PhNH_2* \rightleftarrows PhNH_2 + *$	8.71E-08	0.00E+00	8.71E-08	0.00E+00	0.00	-	–
R18	$PhNO* + PhN* \rightleftarrows PhN(O)NPh* + *$	1.39E-03	1.07E-08	1.39E-03	7.72E-06	-	1.00	119.66
R19	$PhNOH* + PhNOH* \rightleftarrows PhN(OH)N(OH)Ph* + *$	2.90E-10	2.90E-10	1.99E-14	1.00E+00	-	0.00	277.19
R20	$PhNOH* + PhN* \rightleftarrows PhN(OH)NPh* + *$	1.20E-06	3.56E-10	1.20E-06	2.96E-04	-	0.00	197.28
R21	$PhN* + PhN* \rightleftarrows PhNNPh* + *$	1.37E-11	2.44E-14	1.36E-11	1.79E-03	-	0.00	373.03
R22	$PhN(OH)N(OH)Ph* + * \rightleftarrows PhN(OH)NPh* + OH*$	1.99E-14	9.79E-27	1.99E-14	4.93E-13	-	0.00	247.19
R23	$PhN(O)NPh* + H* \rightleftarrows PhN(OH)NPh* + *$	3.30E-04	1.24E-07	3.29E-04	3.77E-04	-	0.00	165.09
R24	$PhN(OH)NPh* + * \rightleftarrows PhNNPh* + OH*$	3.31E-04	1.28E-25	3.31E-04	3.87E-22	-	0.00	343.23
R25	$PhN(O)NPh* + * \rightleftarrows PhNNPh* + O*$	1.97E-12	2.68E-18	1.97E-12	1.36E-06	-	0.00	335.46
R26	$O* + H* \rightleftarrows OH*$	1.35E-07	2.02E-28	1.35E-07	1.50E-21	0.00	0.00	708.01

R27	PhN(O)NPh*⇄ PhN(O)NPh + *	1.06E-03	1.10E-09	1.06E-03	1.04E-06	-	0.00	–
R28	PhNNPh*⇄ PhNNPh + *	3.31E-04	0.00E+00	3.31E-04	0.00E+00	-	0.00	-

Table S6. The coverage ($\theta(j)$) and the degree of thermodynamic rate control ($X_{TRC,\ j}$) of major intermediates *j* at KOH/Pt(111) interface.

Species	$\theta(j)$	$X_{TRC,j}$
H*	1.61E-01	-0.48
$PhNO_2$*	3.34E-09	0.00
PhNOOH*	5.69E-10	0.00
PhNO*	3.28E-05	0.00
O*	8.06E-12	0.00
OH*	1.02E-12	0.00
H_2O*	1.85E-07	0.00
PhNOH*	1.47E-07	0.00
PhN*	8.39E-01	-2.52
PhNH*	1.98E-06	0.00
$PhNH_2$*	1.68E-14	0.00
PhNHO*	9.95E-11	0.00
PhNHOH*	1.11E-05	0.00
PhN(OH)N(OH)Ph*	5.73E-12	0.00
PhN(OH)NPh*	9.62E-06	0.00
PhNNPh*	3.37E-04	0.00
PhN(O)NPh*	5.62E-05	0.00
*	4.03E-06	0.00