

Selective Phenol Hydrogenation to Cyclohexanone over Alkali-Metal-Promoted Pd/TiO₂ in Aqueous Media

*Hu Zhou, Bingbing Han, Tianzhu Liu, Xing Zhong, Guilin Zhuang, Jianguo Wang**

College of Chemical Engineering, Zhejiang University of Technology,
Hangzhou, 310032, China.

Corresponding Author

*E-mail: jgw@zjut.edu.cn. Fax: +86-571-88871037. Tel: +86-571-88871037.

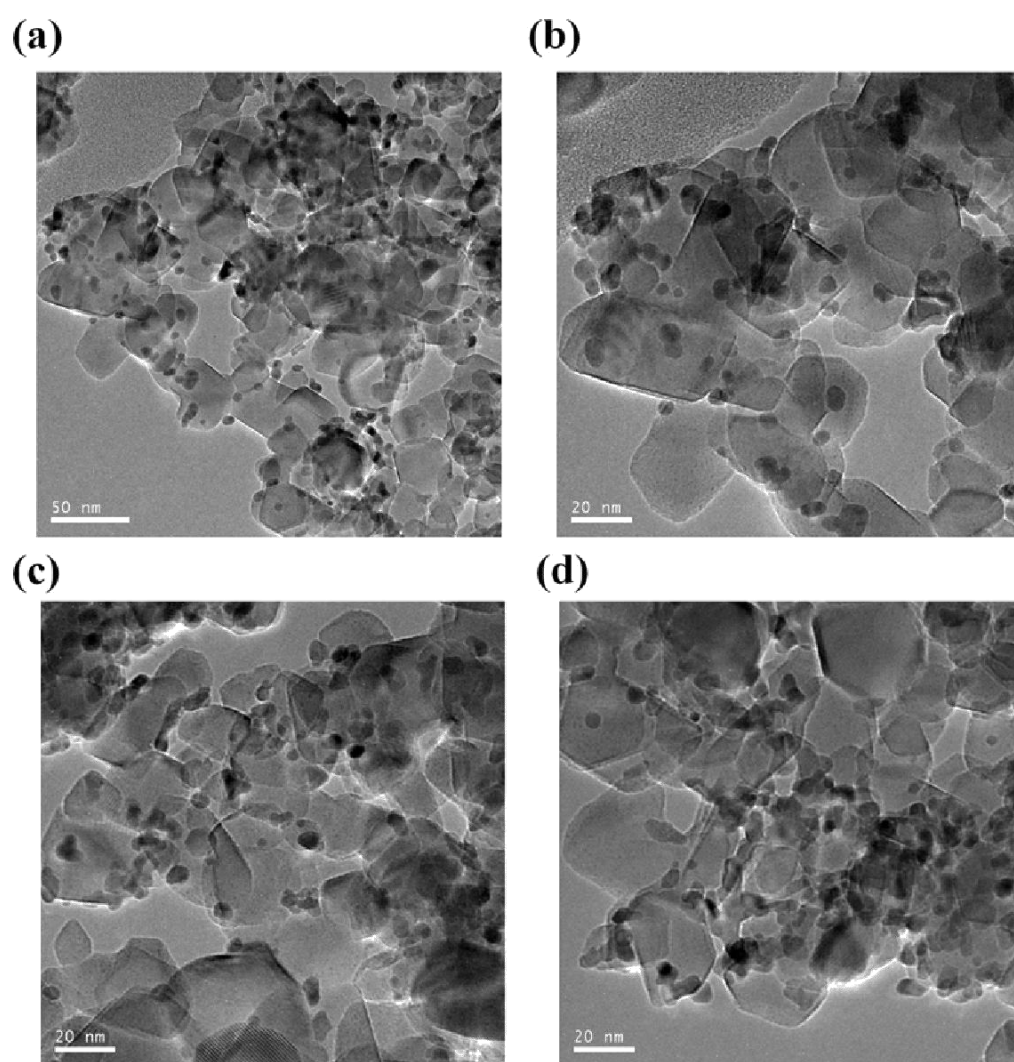


Figure S1 TEM images of Pd/TiO₂ (NH₃·H₂O).

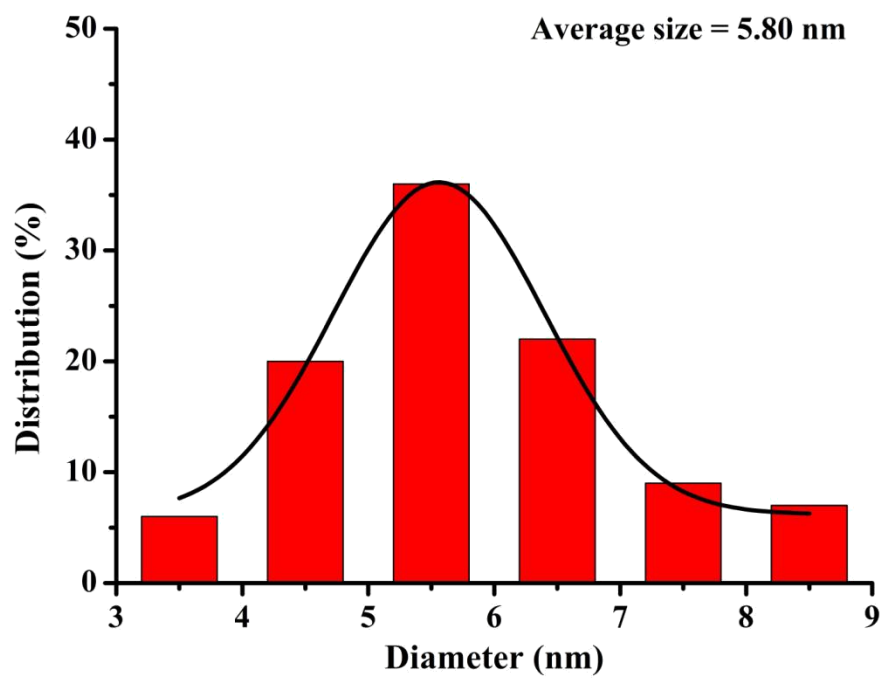


Figure S2 Size distributions of Pd/TiO₂ (NH₃·H₂O).

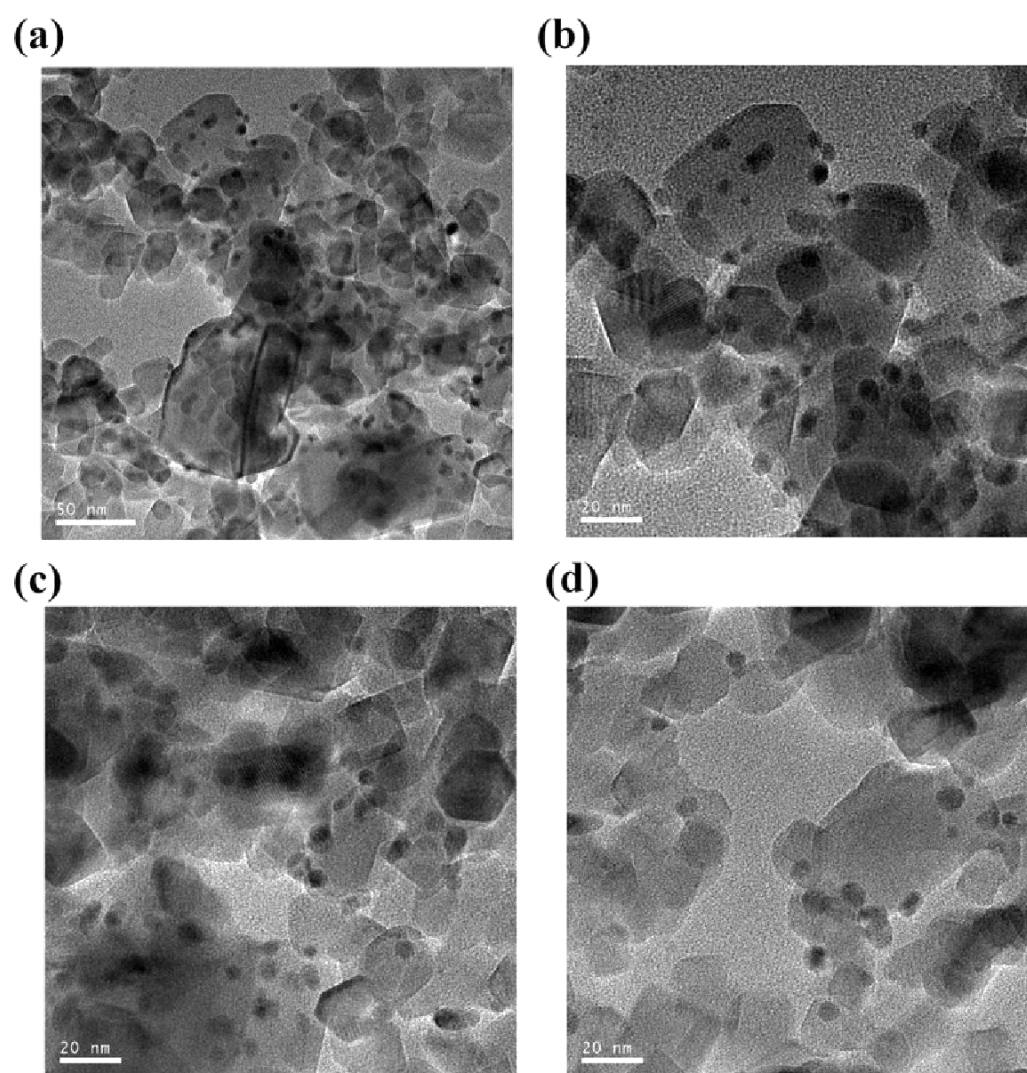


Figure S3 TEM images of Pd/TiO₂.

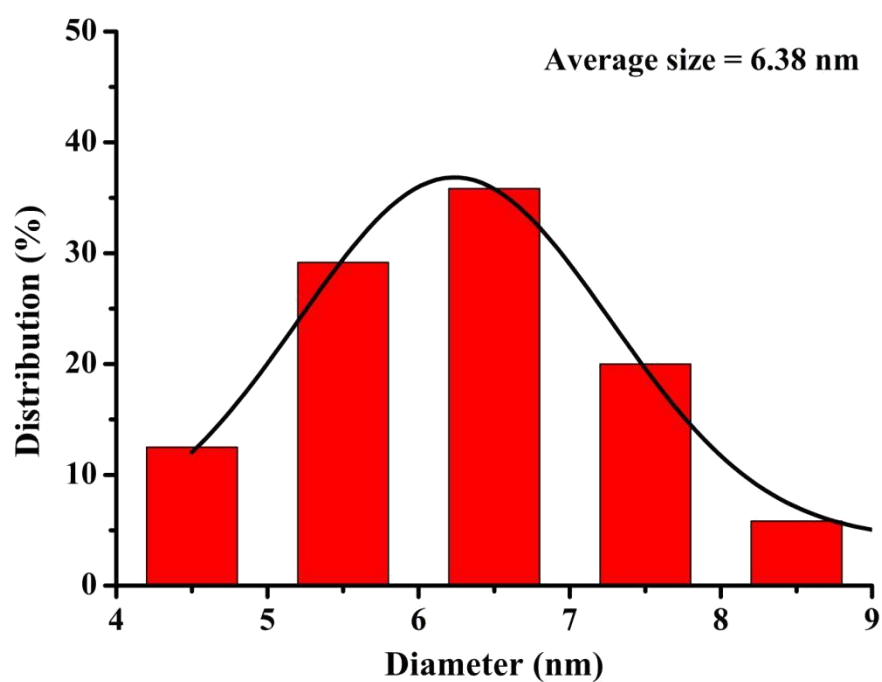


Figure S4 Size distributions of Pd/TiO₂.

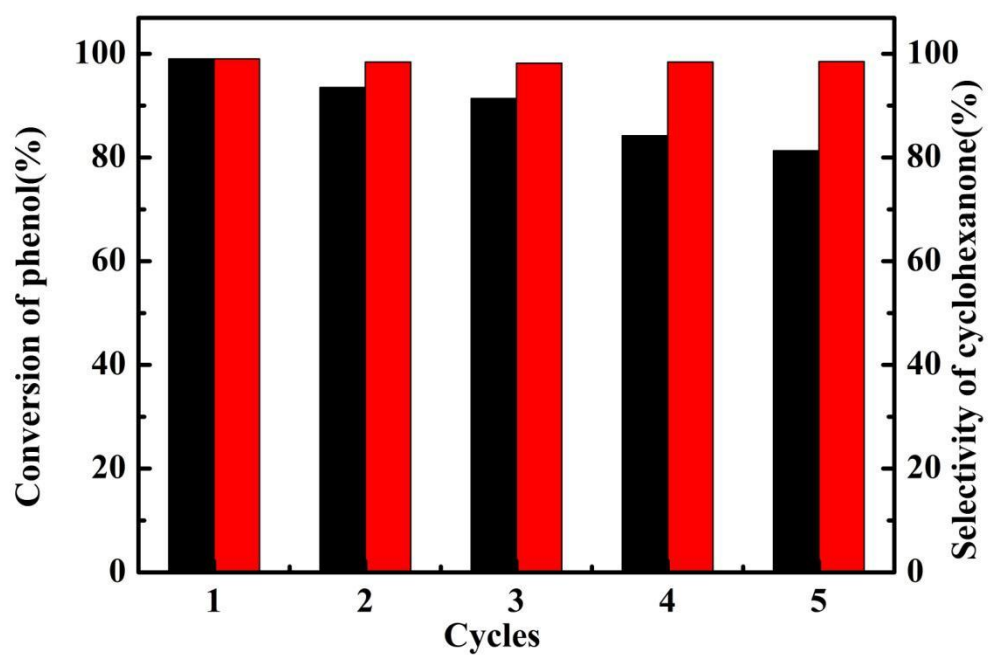


Figure S5 Recycling of the K-Pd/TiO₂(KOH) in the hydrogenation of phenol to cyclohexanone in water at 80 °C and 0.1 MPa .

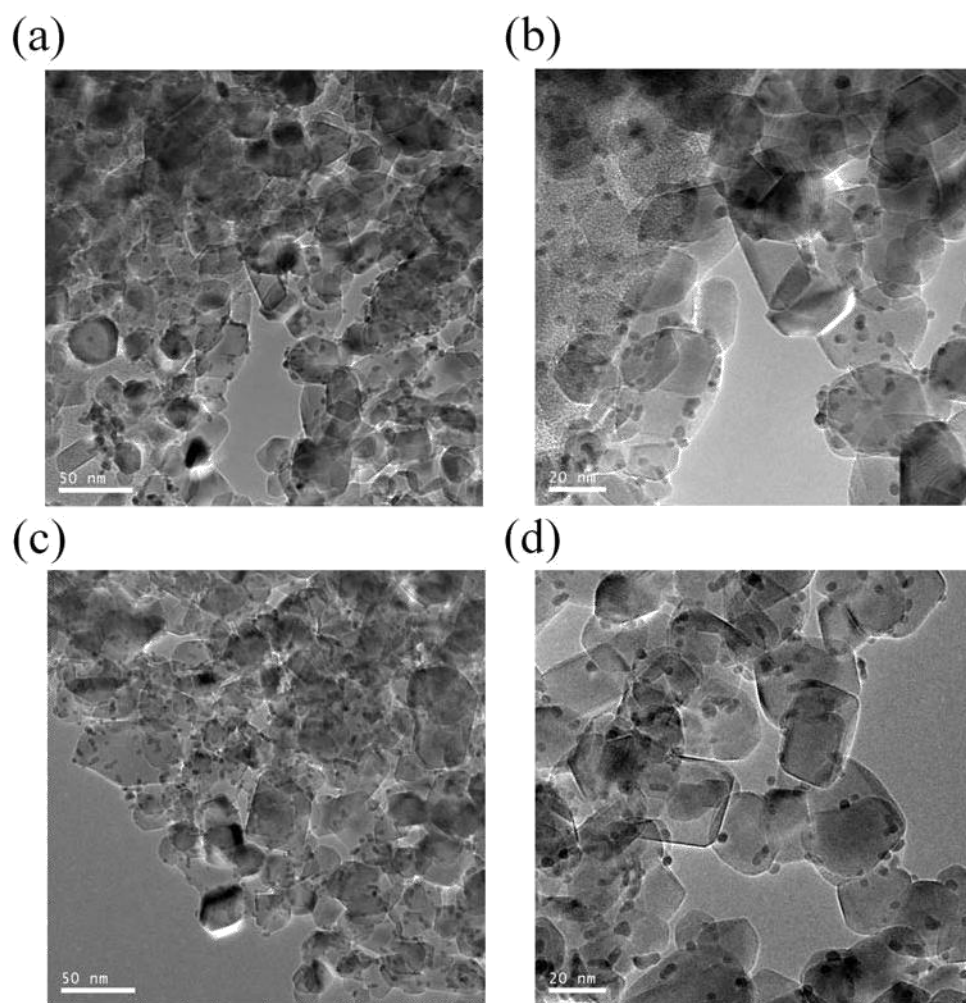


Figure S6 Tem images of K-Pd/TiO₂ catalysts (a), (b) before and (c), (d) after the recycling process.

Table S1 The bulk concentration of Pd and K over the fresh K-Pd/TiO₂(KOH) catalysts and the catalysts after reaction detected by ICP-OES.

Sample	Bulk concentration Pd	Bulk concentration K
K-Pd/TiO ₂ (KOH)_Fresh	4.62%	0.28 %
K-Pd/TiO ₂ (KOH)_After reaction	4.56%	0.03%

Relaxed Atomic Coordinates of the Structures in the Calculated Mechanisms

Section

Notes: Only relaxed atoms were included for systems with adsorbates

Pd(111) slab			
Pd	-0.000	0.000	6.823
Pd	1.393	0.805	4.543
Pd	2.786	0.000	6.823
Pd	4.179	0.805	4.543
Pd	5.572	0.000	6.823
Pd	6.965	0.805	4.543
Pd	8.358	0.000	6.823
Pd	9.751	0.805	4.543
Pd	-1.393	2.413	6.822
Pd	-0.000	3.217	4.542
Pd	1.393	2.413	6.822
Pd	2.786	3.217	4.542
Pd	4.179	2.413	6.822
Pd	5.572	3.217	4.542
Pd	6.965	2.413	6.822
Pd	8.358	3.217	4.542
Pd	-2.786	4.825	6.822
Pd	-1.393	5.629	4.542
Pd	0.000	4.825	6.822
Pd	1.393	5.629	4.542
Pd	2.786	4.825	6.822
Pd	4.179	5.629	4.542
Pd	5.572	4.825	6.822
Pd	6.965	5.629	4.542

Pd	-4.179	7.238	6.822
Pd	-2.786	8.042	4.542
Pd	-1.393	7.238	6.822
Pd	-0.000	8.042	4.542
Pd	1.393	7.238	6.822
Pd	2.786	8.042	4.542
Pd	4.179	7.238	6.822
Pd	5.572	8.042	4.542
Pd	0.000	0.000	0.000
Pd	-0.000	1.608	2.275
Pd	2.786	0.000	0.000
Pd	2.786	1.608	2.275
Pd	5.572	0.000	0.000
Pd	5.572	1.608	2.275
Pd	8.358	0.000	0.000
Pd	8.358	1.608	2.275
Pd	-1.393	2.413	0.000
Pd	-1.393	4.021	2.275
Pd	1.393	2.413	0.000
Pd	1.393	4.021	2.275
Pd	4.179	2.413	0.000
Pd	4.179	4.021	2.275
Pd	6.965	2.413	0.000
Pd	6.965	4.021	2.275
Pd	-2.786	4.825	0.000
Pd	-2.786	6.434	2.275
Pd	-0.000	4.825	0.000
Pd	-0.000	6.434	2.275
Pd	2.786	4.825	0.000
Pd	2.786	6.434	2.275

Pd	5.572	4.825	0.000
Pd	5.572	6.434	2.275
Pd	-4.179	7.238	0.000
Pd	-4.179	8.847	2.275
Pd	-1.393	7.238	0.000
Pd	-1.393	8.847	2.275
Pd	1.393	7.238	0.000
Pd	1.393	8.847	2.275
Pd	4.179	7.238	0.000
Pd	4.179	8.847	2.275

K-Pd(111)

K	-0.137	6.312	9.645
Pd	-0.001	-0.001	6.822
1.393	0.804	4.543	Pd
2.786	-0.001	6.825	Pd
4.180	0.804	4.545	Pd
5.572	-0.006	6.833	Pd
6.964	0.804	4.545	Pd
8.356	-0.002	6.825	Pd
9.750	0.804	4.544	Pd -
1.393	2.413	6.826	Pd -
0.000	3.210	4.535	Pd
1.392	2.412	6.825	Pd
2.786	3.217	4.544	Pd
4.179	2.412	6.822	Pd
5.572	3.216	4.541	Pd
6.965	2.412	6.823	Pd
8.358	3.217	4.545	Pd -
2.781	4.828	6.835	

Pd -1.396 5.628 4.535
Pd 0.000 4.817 6.801
Pd 1.396 5.629 4.537
Pd 2.781 4.827 6.833
Pd 4.179 5.628 4.544
Pd 5.572 4.825 6.822
Pd 6.965 5.629 4.545
Pd -4.178 7.237 6.826
Pd -2.791 8.044 4.536
Pd -1.399 7.241 6.805
Pd 0.001 8.044 4.538
Pd 1.394 7.238 6.817
Pd 2.789 8.044 4.539
Pd 4.177 7.237 6.825
Pd 5.571 8.041 4.543
Pd 0.000 0.000 0.000
Pd -0.000 1.608 2.275
Pd 2.786 0.000 0.000
Pd 2.786 1.608 2.275
Pd 5.572 0.000 0.000
Pd 5.572 1.608 2.275
Pd 8.358 0.000 0.000
Pd 8.358 1.608 2.275
Pd -1.393 2.413 -0.000
Pd -1.393 4.021 2.275
Pd 1.393 2.413 -0.000
Pd 1.393 4.021 2.275
Pd 4.179 2.413 0.000
Pd 4.179 4.021 2.275
Pd 6.965 2.413 0.000

Pd	6.965	4.021	2.275
Pd	-2.786	4.825	-0.000
Pd	-2.786	6.434	2.275
Pd	-0.000	4.825	-0.000
Pd	-0.000	6.434	2.275
Pd	2.786	4.825	0.000
Pd	2.786	6.434	2.275
Pd	5.572	4.825	0.000
Pd	5.572	6.434	2.275
Pd	-4.179	7.238	-0.000
Pd	-4.179	8.847	2.275
Pd	-1.393	7.238	-0.000
Pd	-1.393	8.847	2.275
Pd	1.393	7.238	-0.000
Pd	1.393	8.847	2.275
Pd	4.179	7.238	0.000
Pd	4.179	8.847	2.275

Phenol on Pd(111)

H	-0.005	4.824	9.441
H	0.010	2.347	9.314 H
2.178	1.140	9.335	H
4.268	4.879	9.296	H
2.119	6.091	9.285	H
5.288	2.643	9.485	C
0.856	4.334	8.971	C
0.909	2.887	9.006	C
2.151	2.179	9.000	C
3.423	2.886	8.997	C
3.372	4.346	8.966	C
2.120	5.040	8.985	

O 4.419 2.256 9.727
Pd -0.025 -0.036 6.794
Pd 1.395 0.818 4.545 Pd
2.787 -0.046 6.792 Pd
4.174 0.829 4.557 Pd
5.558 0.023 6.810 Pd
6.959 0.810 4.534 Pd
8.340 0.016 6.810 Pd
9.751 0.806 4.528 Pd -
1.449 2.401 6.797 Pd
0.014 3.215 4.574 Pd
1.332 2.331 6.913 Pd
2.776 3.224 4.570 Pd
4.123 2.449 6.946 Pd
5.551 3.212 4.560 Pd
6.944 2.422 6.817 Pd
8.355 3.218 4.530 Pd -
2.778 4.824 6.818 Pd -
1.359 5.611 4.575 Pd
0.025 4.812 6.969 Pd
1.401 5.622 4.570 Pd
2.829 4.931 6.896 Pd
4.173 5.625 4.541 Pd
5.617 4.852 6.798 Pd
6.975 5.624 4.528 Pd -
4.164 7.232 6.809 Pd -
2.775 8.039 4.527 Pd -
1.386 7.235 6.814 Pd -
0.002 8.048 4.529 Pd
1.376 7.300 6.794

Pd 2.787 8.045 4.527
Pd 4.203 7.286 6.792
Pd 5.583 8.039 4.519

Phenol on K-Pd(111)

H 6.968 2.454 9.448 H
4.857 1.166 9.300 H
2.702 2.353 9.316 H
4.755 6.120 9.307 H
6.922 4.941 9.299 H
2.232 5.775 9.314 C
6.102 2.935 8.977 C
4.846 2.219 9.008 C
3.591 2.904 8.998 C
3.509 4.357 8.965 C
4.782 5.077 8.981 C
6.032 4.382 9.000 O
2.441 4.903 9.729 K -
0.073 3.646 9.673
Pd -0.030 0.017 6.824
Pd 1.388 0.800 4.528
Pd -2.823 9.609 6.799
Pd 4.178 0.816 4.549
Pd -0.003 9.601 6.798
Pd 6.955 0.832 4.566
Pd 8.336 0.021 6.826
Pd 9.740 0.808 4.537
Pd -1.424 2.420 6.820
Pd -0.011 3.216 4.525
Pd 1.324 2.398 6.792

Pd 2.794 3.213 4.560
Pd 4.102 2.321 6.914
Pd 5.556 3.225 4.580
Pd 6.912 2.451 6.972
Pd 8.327 3.214 4.565
Pd -2.747 4.851 6.811
Pd -1.397 5.628 4.522
Pd -0.001 4.839 6.779
Pd 1.428 5.618 4.566
Pd 2.808 4.795 6.944
Pd 4.184 5.625 4.564
Pd 5.600 4.937 6.911
Pd 6.951 5.623 4.552
Pd -4.164 7.285 6.800
Pd -2.780 8.038 4.523
Pd -1.385 7.232 6.821
Pd 0.006 8.039 4.532
Pd 1.394 7.230 6.839
Pd 2.778 8.051 4.538
Pd 4.150 7.300 6.805
Pd 5.568 8.045 4.533

Cyclohexanone on Pd(111)

H 3.628 2.470 12.363
H 3.407 0.318 11.105 H
5.743 0.200 10.080 H
6.026 4.453 10.073 H
3.677 3.803 9.587 H
2.282 2.569 11.222 H
3.512 1.184 9.566

H 5.724 0.964 11.692
H 5.921 3.696 11.684 H
3.710 4.647 11.142 C
3.379 2.494 11.287 C
3.851 1.201 10.621 C
5.389 1.076 10.644 C
6.042 2.315 10.086 C
5.562 3.632 10.639 C
4.021 3.720 10.636 O
6.918 2.246 9.208 Pd
0.003 -0.001 6.790 Pd
1.394 0.807 4.511 Pd
2.784 -0.000 6.792 Pd
4.179 0.806 4.508 Pd
5.565 -0.012 6.778 Pd
6.966 0.818 4.528 Pd
8.366 -0.011 6.783 Pd
9.752 0.806 4.510 Pd -
1.378 2.414 6.782 Pd -
0.002 3.219 4.508 Pd
1.393 2.415 6.788 Pd
2.788 3.220 4.507 Pd
4.164 2.414 6.779 Pd
5.582 3.214 4.526 Pd
6.964 2.415 6.871 Pd
8.349 3.214 4.528 Pd -
2.781 4.838 6.785 Pd -
1.393 5.629 4.510 Pd
0.003 4.828 6.790 Pd
1.394 5.631 4.511

Pd	2.785	4.827	6.792
Pd	4.179	5.629	4.508
Pd	5.568	4.839	6.780
Pd	6.966	5.632	4.509
Pd	-4.178	7.242	6.790
Pd	-2.785	8.044	4.512
Pd	-1.393	7.238	6.789
Pd	0.002	8.044	4.508
Pd	1.393	7.235	6.790
Pd	2.785	8.045	4.510
Pd	4.180	7.238	6.789
Pd	5.572	8.043	4.511

Cyclohexanone on K-Pd(111)

H	6.335	3.026	11.959
H	6.856	5.183	10.796
H	4.574	6.325	10.995
H	2.610	2.561	11.051
H	4.562	2.444	9.509
H	6.885	2.714	10.302
H	5.767	4.755	9.474
H	4.997	5.321	12.400
H	3.692	2.821	12.437
H	4.852	1.339	10.855
C	6.064	3.151	10.894
C	5.928	4.637	10.565
C	4.756	5.290	11.320
C	3.470	4.509	11.206
C	3.566	3.011	11.353
C	4.764	2.405	10.598
O	2.383	5.074	11.031

K 0.450 6.134 9.746
Pd 0.001 -0.000 6.824
Pd 1.395 0.804 4.544
Pd 2.788 -0.002 6.826
Pd 4.180 0.806 4.545
Pd 0.001 9.646 6.830
Pd 6.965 0.804 4.544
Pd 8.359 -0.001 6.825
Pd 9.751 0.804 4.544
Pd -1.391 2.413 6.826
Pd 0.001 3.210 4.534
Pd 1.392 2.414 6.826
Pd 2.787 3.216 4.544
Pd 4.179 2.413 6.829
Pd 5.572 3.217 4.543
Pd 6.968 2.411 6.821
Pd 8.358 3.218 4.543
Pd -2.781 4.827 6.829
Pd -1.396 5.631 4.537
Pd -0.002 4.819 6.795
Pd 1.396 5.628 4.532
Pd 2.781 4.828 6.827
Pd 4.180 5.629 4.544
Pd 5.572 4.826 6.829
Pd 6.965 5.628 4.544
Pd -4.175 7.238 6.825
Pd -2.787 8.043 4.542
Pd -1.390 7.236 6.827
Pd -0.003 8.044 4.537
Pd 1.397 7.243 6.799

Pd 2.792 8.045 4.535

Pd 4.178 7.238 6.825

Pd 5.574 8.041 4.544

TS1 Pd(111)

H -0.405 4.396 9.249 H

0.319 2.065 9.292 H

2.229 2.526 10.804 H

3.706 5.754 9.343 H

1.267 6.242 9.208 H

5.299 3.999 9.495 H

2.844 1.556 9.461 C

0.629 4.171 8.955 C

1.092 2.784 8.993 C

2.416 2.540 9.704 C

3.416 3.620 9.465 C

3.007 4.930 9.169 C

1.601 5.217 9.030 O

4.674 3.305 9.813 Pd

5.564 9.637 6.789 Pd

1.394 0.829 4.537 Pd

2.782 -0.000 6.790 Pd

4.173 0.815 4.511 Pd

5.561 0.012 6.788 Pd

6.962 0.808 4.516 Pd

8.349 0.010 6.788 Pd

9.756 0.802 4.505 Pd

9.707 2.397 6.764 Pd

0.001 3.220 4.523 Pd

1.341 2.375 6.929 Pd

2.771 3.230 4.563

Pd	4.179	2.410	6.781
Pd	5.568	3.222	4.509
Pd	6.956	2.421	6.792
Pd	8.357	3.224	4.509
Pd	-2.791	4.830	6.794
Pd	-1.363	5.618	4.549
Pd	0.016	4.786	6.903
Pd	1.406	5.621	4.551
Pd	2.820	4.879	6.944
Pd	4.166	5.623	4.530
Pd	5.600	4.843	6.775
Pd	6.974	5.636	4.508
Pd	-4.168	7.243	6.797
Pd	-2.780	8.044	4.515
Pd	-1.395	7.242	6.791
Pd	-0.000	8.044	4.507
Pd	1.381	7.290	6.773
Pd	2.786	8.044	4.504
Pd	4.200	7.275	6.773
Pd	5.578	8.043	4.506
TS1 K-Pd(111)			
H	5.966	4.381	9.258
H	5.206	2.059	9.324
H	3.280	2.536	10.815
H	1.862	5.781	9.339
H	4.314	6.248	9.219
H	0.254	3.983	9.169
H	2.691	1.573	9.440
C	4.924	4.168	8.982
C	4.445	2.785	9.013

C 3.107 2.555 9.712
C 2.128 3.647 9.434
C 2.559 4.953 9.189
C 3.969 5.225 9.054
O 0.817 3.374 9.728
K 10.351 1.055 9.650
Pd -5.553 9.650 6.780
Pd 1.403 0.813 4.522
Pd -2.784 9.644 6.815
Pd 4.180 0.824 4.561
Pd 0.011 9.635 6.814
Pd 6.965 0.802 4.528
Pd 8.372 0.008 6.823
Pd 9.751 0.807 4.525
Pd -1.387 2.423 6.792
Pd 0.006 3.223 4.520
Pd 1.391 2.403 6.793
Pd 2.803 3.230 4.578
Pd 4.229 2.371 6.949
Pd 5.572 3.217 4.547
Pd 7.013 2.392 6.795
Pd 8.356 3.223 4.519
Pd -2.780 4.824 6.818
Pd -1.404 5.634 4.525
Pd -0.034 4.835 6.808
Pd 1.403 5.623 4.553
Pd 2.752 4.876 6.956
Pd 4.166 5.620 4.574
Pd 5.559 4.782 6.923
Pd 6.937 5.615 4.570

Pd -4.176 7.238 6.815
Pd -2.792 8.042 4.531
Pd -1.403 7.238 6.816
Pd -0.008 8.043 4.525
Pd 1.373 7.273 6.797
Pd 2.786 8.041 4.530
Pd 4.194 7.289 6.808
Pd 5.572 8.033 4.522

TS3 Pd(111)

H -1.315 4.700 9.352
H 9.965 2.226 9.462 H
1.008 1.065 9.180 H
2.752 4.714 9.855 H
0.750 6.032 9.324 H
3.423 4.979 8.307 C -
0.392 4.218 9.022 C -
0.356 2.771 8.984 C
0.935 2.122 8.904 C
2.194 2.870 8.907 C
2.136 4.362 9.010 C
0.805 4.994 8.983 O
3.341 2.279 8.995
Pd 5.554 9.585 6.773
Pd 1.384 0.796 4.509
Pd -2.789 9.587 6.777
Pd 4.170 0.813 4.544
Pd 5.577 0.002 6.798
Pd 6.961 0.806 4.529
Pd 8.359 0.015 6.805

Pd 9.749 0.826 4.550
Pd -1.338 2.423 6.983
Pd -0.009 3.227 4.547
Pd 1.391 2.325 6.786
Pd 2.772 3.213 4.546
Pd 4.188 2.369 6.916
Pd 5.547 3.199 4.580
Pd 6.984 2.408 6.822
Pd 8.369 3.202 4.565
Pd -2.836 4.833 6.798
Pd -1.392 5.616 4.549
Pd -0.040 4.903 6.932
Pd 1.376 5.617 4.554
Pd 2.762 4.856 6.863
Pd 4.150 5.615 4.551
Pd 5.561 4.825 6.837
Pd 6.945 5.606 4.523
Pd -4.200 7.215 6.798
Pd -2.800 8.027 4.512
Pd -1.423 7.258 6.792
Pd -0.011 8.043 4.515
Pd 1.380 7.302 6.779
Pd 2.780 8.047 4.519
Pd 4.169 7.251 6.811
Pd 5.554 8.029 4.511

TS3 K-Pd(111)

H 7.241 2.535 9.279 H
5.320 0.968 9.173 H
3.013 1.826 9.490

H 4.875 5.437 10.419
H 6.915 4.947 9.224 H
4.320 5.679 8.781 C
6.274 2.918 8.922 C
5.130 2.034 9.011 C
3.807 2.525 9.218 C
3.598 3.902 9.643 C
4.725 4.891 9.471 C
6.039 4.350 8.940 O
2.541 4.275 10.205 K
0.482 5.657 9.769 Pd
5.553 9.653 6.802 Pd
1.389 0.806 4.527 Pd -
2.814 9.626 6.799 Pd
4.177 0.826 4.561 Pd
0.000 9.611 6.795 Pd
6.959 0.828 4.547 Pd
2.781 9.654 6.801 Pd
9.742 0.806 4.522 Pd -
1.400 2.415 6.803 Pd -
0.002 3.212 4.516 Pd
1.347 2.412 6.804 Pd
2.802 3.207 4.567 Pd
4.107 2.389 7.012 Pd
5.551 3.211 4.561 Pd
6.947 2.441 6.898 Pd
8.338 3.214 4.541 Pd -
2.734 4.855 6.789 Pd -
1.398 5.637 4.514 Pd -
0.008 4.825 6.762

Pd 1.402 5.633 4.511

Pd 2.750 4.851 6.778

Pd 4.202 5.618 4.551

Pd 5.655 4.846 6.889

Pd 6.961 5.627 4.526

Pd -4.170 7.261 6.795

Pd -2.784 8.048 4.524

Pd -1.386 7.241 6.818

Pd -0.002 8.054 4.523

Pd 1.391 7.244 6.799

Pd 2.785 8.046 4.518

Pd 4.172 7.252 6.796

Pd 5.569 8.041 4.522