wcasing research from P… …of
emistry, Fuzhou Universi…

ective hydrogenation o… …by a single
atom anchored on gr… …of dynamics

sed on density functi… …ns, a reaction
chanism is propose… …ydrogenation
utadiene catalyz… …m Pd catalyst
raphene. Impor… …electivity towa…
ributed to the … …-state dynamic…
ogenation ste… …us exclusively t…
e product. T… …ical insight un…
rtance of … …in heterogene…
anism fo… …y may be ope…
tic proc… …offers an ef… …g principle
talyze… …enous che… …ansformations.

See Sen Lin, Hua Guo *et al.*, *Chem. Sci.*, 2018, **9**, 5890.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemical-science

Registered charity number: 207890

Chemical Science

EDGE ARTICLE

Cite this: *Chem. Sci.*, 2018, **9**, 5890

Selective hydrogenation of 1,3-butadiene catalyzed by a single Pd atom anchored on graphene: the importance of dynamics†

Yn n Fqn , [a] Lnqn Zq , [b] Qan Wan, [a] Sqn Ln *[ab] and H a G *[b]

Tq ac -q c , ac n qan , and d c qc q nd a d qna n 1,3-b adqn a n aqd n fi nc q anq qn n -a Pd ca a anq d n qq. Dqn nc na q ca a n q a q n -π-ad bqd acan ndq q a q d qna n b Pd-ac aqd H_2. I an , q q a qc aqd 1-b qn a b qd q -qn n- aq d na c n q qc nd a d qna n q , q qad q c , q q dq n q d c. Tq d na ca qn a dq q q qc qnq qn ca d 1-b qn ad n n Pd, q d qn a qad c q q d qna n b anq and bq , nc n qn q q qn a bq an . Tq n , ndq c q q an nc d na c n q qn ca , q q a ab qn ndq a c aqd.

Rqq qd 15 Fb a 2018
Acq qd 14 J n 2018

DOI: 10.1039/c8 c00776d

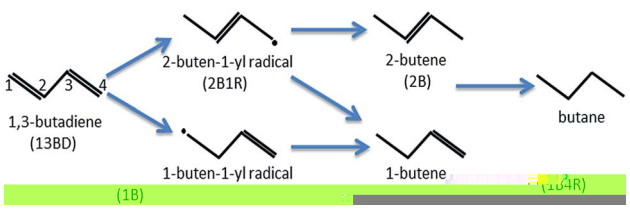
rsc.li/chemical-science

Introduction

1,3-B ad (CH_2=CH–CH=CH_2) d c ac a a ca a d a a a , ad a a ad c acc d ca a c d a .[1] I ca a d d a 1,3-b ad , a d c , c d b a d b a , ca b d c d ca- ca H –P a c a (Sc 1). D ac , c d ca a d c a a (*e.g.*, Pd P) a a c a c .[2–6] I d ab d ac ca a c a d c fic d c , ab 1-b (CH_2=CH–CH_2–CH_3), c ca b d a a d c b - a ac . T c d c a c ca a.

S -a ca a (SAC) a c d a a a ad a ca a ca a a c ca a , b ca a c ffic c a d ac c a .[7–9] H ac a d c SAC d a 1,3-b ad a b d b a . Z a *et al.*,[10] a , d a d a 1,3-b ad A /Z O_2 ca a a 100% c a d b a a b a d A^{3+} Z O_2 ac . S a d c d a a d P a a C ac ca a ca a d d c d b ad d a- ac c a d b .[11] M c , b -d a a a , a ca d d Pd a b d b Ya *et al.*[12] b a 100% b c 1,3-b ad d - a 95% c a 50 °C.

T b d c SAC-ca a d b ad d - a ca b a a d a a b ac a a a ca d d SAC ca ab d -π-ad - c a ac a a c ,[13–17] c a a a a a ac . Ra , a c SAC c a -π- ad a d a d a C=C d b b d a a . N , SAC ca a c c a a ft c a ca , a ca c . I d d, a a



Scheme 1 P a q a a 1,3-b adqn d qna n *via* q H –P an q an .

[a]*State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, China. E-mail: slin@fzu.edu.cn*
[b]*Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, USA. E-mail: hguo@unm.edu*

† E c c a a (ESI) a a ab . S DOI: 10.1039/c8 c00776d

d a c a d a a ca ad c . T c d c a b a d a c c b ac d a .

T a ad d a d c , ca a . O P (111) a d Pd(111) ac , a , d c a (DFT) ca c a b Sa a d c a a d a c ca b a b d d ff c ad b 1,3-b ad (ad d C=C d b b d) a d b (a ad d C=C d b b d) a a d ff ab a ad ca d a .[14] H , c a c a a SAC b ca ad ac a d a b c d ff , ac ac SAC ca b d a C=C d b b d.

L a d c c a d c 1,3-b ad ca a d b a A SAC d b a Z O_2 ac .[18] T DFT ca c a a d a fi d - a a OH d ac d b ab ac H ad b d A , b d a a d b a a d a a a ba a fi d a . A a a a d a ff d, b d c d c a d.[18] W d c ca a c c a a SAC d , d b a cab SAC a [11] 2D a a ,[12] a OH a b a .

I , b c b a c DFT ca c a *ab initio* c a d a c (AIMD)[19] d c d a c[20] - a , 1,3-b ad d a a a d Pd SAC (Pd_1/ a) a a d. T a ff a c a d - a d c b ad d a a c - a -d fi d SAC.[12] O DFT ca c a a a c a a c - c SAC a d a ca a c a a , c a d b c a b a . P a , c a d b AIMD a b - a - a d a c c d d a , c 1-b d b a c a a d a Pd ffic c c ad . T d a ca a a a a a b d a C=C d b b d 1-b Pd, c d ad a d a b a a d b c a b a .

T a c d a c ca a a c a ac d c a . F a da a d c a c , d a d a a d ff ac a (b a *vs.* a - a) d c a d ff fficac .[21–23] H , a b a fl c d a c d c b a c ac c . T d a ca d c d a d c c - a a dd c a c c a ac (PES) d c a c a a d ac , b a d c b a c . S c fica - ca d a ca a ad ,[24] a ac d c ac c d a (IRC) PES, c d fi a ac a a a a d a d c . H , c a a a d ca d c d ca a ca ba d c a b a d a c ca ac , c a da c IRC aft a ac a a a ad " c d" d c .[25–31] T ac -IRC ac c , c acc d b PES a . I a d a c c a ac a ac , a a , c a d aft a a a a ca ad a c a a . I d c d , d a ca d c d a a 1,3-b ad d a a a a a d ac - ca a . U d c c c a c , d a c a b c c d d.

Computational details

DFT

A - a d d c a (DFT) ca c a ca d V a *Ab initio* S a Pac a (VASP)[32,33] ad -c c d P d –B –E (PBE) c a .[34] T a c c d c b d a a - a ba a c ff 400 V, c c a a d c a d- a d.[35] T a c c d d ac b G - ca c [36] a d a d Waa c c a d d Tab S1.† A b c c a $a = 9.84$ Å (a x d c-), $b = 12.78$ Å (fi a y d c) a d $c = 30.0$ Å d. A 2 × 2 × 1 M –Pac k- d[37] ad d B a a d c c . T d b c a ad a a c a a a 0.03 V $Å^{-1}$, c a a ca a a d ad ba a d. T c b a d d a c ba d (CI-NEB)[38,39] a ac a d d ac a a d b a a a a d a a c a ac c ca a a d a a .

AIMD simulations

T - a - a d a c , *ab initio* c a d a c (AIMD) a [19] ca d VASP a a d c b d ab . A c a ac c a c fi a a d b a a a a a d d b NEB ca c a a c c . F a c c d a a a a a , b a c a a d a d a d ca d a a a

c 300 K. W a d c ca ca a a c d a c a d a a a ,[40,41] c a b a d d a a a - d H a a d a a . T c ac a a d a 300 K. T a c a a d a c - ca ca (NVE) b a - a d VASP, a a a a 2 a d a 0.5 . T a a c d ~20 V a a c .

Results and discussion

Model of the Pd_1/graphene SAC

H a Pd SAC a fi a d a c d a d ca a c c a c d a 1,3-b ad . T d d d ba d a Ya *et al.*,[12] d ab ca Pd– a a X- a c c (XPS), ca a c c c (STEM), a d d d X- a ab fi c (EXAFS) a - . T a da a a a ca d d Pd c a a c d a a- c d a C a d O a . O d Pd_1/ a SAC c Pd–C a d Pd–O b d , a F . 1, c b d fi - a EXAFS c .[12] T c O_a, c b d Pd a a d a , c - d a c c a d b da a .[12] T Pd a a c d a C_a. T c a-c d a Pd, c (O_b a d $O_{b'}$) a c d d (F . 1a), c a ab d aft a afl ac ac a a d d a c a d Pd c .[12] F , d a a add a d d a a ca b a a d c d a d a add a Pd–C b d . T C–O–C d d a a d a a a c a a a ca a c . A Tab 1, d SAC d b d a a d a

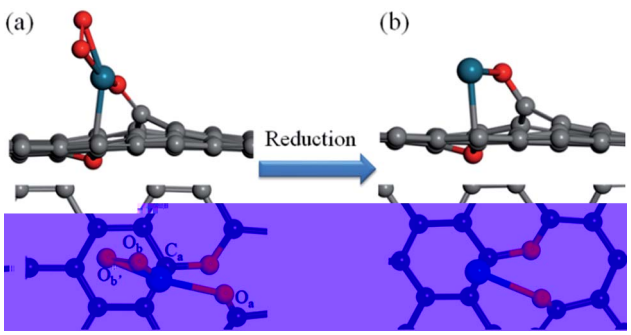


Fig. 1 S d a d ۱ ۹ ۹ Pd_1/ ◀ a ۹ ۹ SAC (a) b ۹ ◀ a d (b) a ۹◀◀d c ∩. C ◀ ۹ ۹: C, ◀ ; O, ◀d; Pd, b ۹.

Table 1 C ۱ a◀ ∩ ca ç a ۹d a d ۱ ۹a ◀d b ∩ d ۹ ∩ a ۹ ۹ Pd SAC ∩ ◀ a ۹ ۹

B d	T .	E .[12]
Pd–O_a	2.09	2.05
P–O_b	2.05	2.07
Pd–$O_{b'}$	2.00	2.07
Pd–C_a	2.25	2.00

a Pd–C a d Pd–O b d fi c d - a .[12] I add , c c d ca b a d a c a a EXAFS.[12] T Bad c a a a d ca a c a Pd a +0.69*e*, c a b - a a a d Pd a a ac a c a d.[12]

T SAC c d c d ab a a ac ca a ba d a DFT ca c a d a ac ( ), ab b ca c ca a-c d a d Pd. I d a ca a a - a d 10% H_2 A a 150 °C, c c d c c ab d c O b d d Pd. T b , ac (1)–(3) a a d ca :

$$PdO_2/graphene + H_2 \rightarrow Pd(OH)_2/graphene \quad (1)$$

$$Pd(OH)_2/graphene + H_2 \rightarrow PdOH/graphene + H_2O \quad (2)$$

$$PdOH/graphene + H_2 \rightarrow Pd/graphene + H_2O \quad (3)$$

I a d DFT ca c a a ac (1) a a a c −3.28 V, d ca a Pd b d O ca b ad d c d d (OH) c H_2 (F . S1 ESI†). T a d ca b d c d b a add a H_2 c H_2O c ac (2) a d (3). T ac a ca c a d a ba , 0.98 a d 0.63 V, c (F . S2†). T fi a ac a d SAC a a a d Pd a a c d a (F . 1b).

T Pd_1/ a SAC d d b a b ad a d ca a . T SAC a ab ab , a Pd b d −1.87 V c ca c a d $E_b = E_{Pd-} - E - E_{Pd}$ E_{Pd-} Pd-SAC, E b Pd a a d E_{Pd} Pd a . T a Pd ad (−1.75 V) C O_2(111).[42] T Pd a a a c a +0.30*e*, a fica ca c c a ac d c a a a d .

Adsorption of pertinent species

B a ac c a , ad b a H_2, 1,3-b ad (13BD), 1-b (1B), a d b a d d (F . 2). T d c d ad b

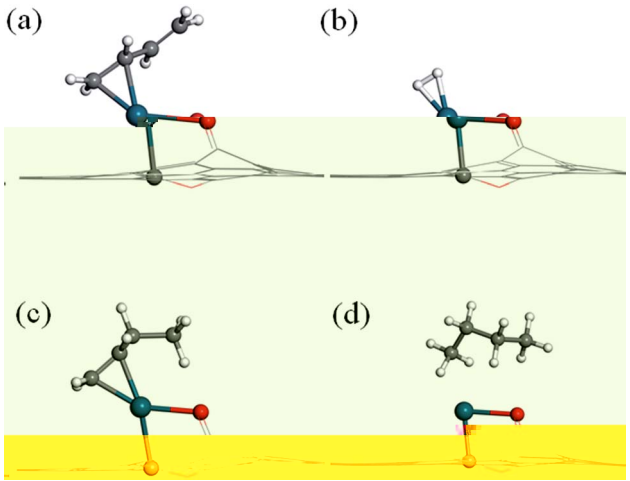


Fig. 2 Ad ◀ n ◀c◡ ◀ (a) 1,3-b ad ◉, (b) H_2, (c) 1-b ◉ and (d) b ◉ n ◉ Pd_1/◀ ◉ ◉ SAC. C ◀ ◉ ◉: C, ◀ ; O, ◀d; Pd, b ◉; H, ◉ . A ◉ ◉ a ◉ ◀d a ◉d n ◉ ◉ c◉ ◉ ◉ ca a c c◉n ◉◀and ◉ ◉ ad ◀ba ◉ .

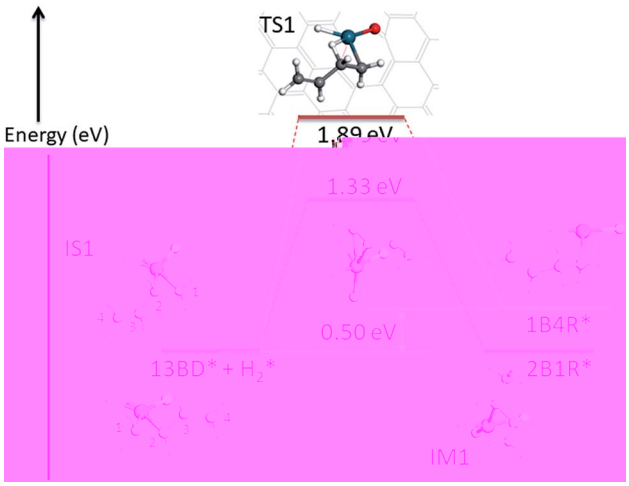


Fig. 3 En◉◀◉ c and ◀c◡ ◀ a na◀ n a n ◉ ◉◀ac- n a◉ a ◀◉ ◉ fi◀ ◉ d◀ ◉n a n ◉ 1,3-b ad◉ ◀ 1-b ◉ n ◉ Pd_1/◀ ◉ ◉ SAC. IS: n a a ◉; TS: ◀n n a ◉; IM: n ◉◀ ◉d a ◉ a ◉; FS: fin a ◉. T◉ a ◉ c ◀ ◉ ◉ a n F . 2 ◡ ◉d.

Pd Pd–H d a c 1.73 a d 1.74 Å, c , a d a b d −0.78 V. T b d H_2 ab 0.87 Å, c 0.12 Å a a a d a . T , d ca b c d d ac a d b Pd a , b d c a d.

F 1,3-b ad , a d *trans*-ca c a b ca d a a a . S c SAC-ca a d d a a , , da a d ff c c d b *cis* a d *trans* b ca c d d c (*cis* a d *trans*-1-b) a a d b a( ) a a d dd C–C b d. A c d, C=C d b b d ca ab b d Pd a , a C=C d b b d d a ac . T ad b d C=C d b b d 1.41 Å, c a d b 0.07 Å a a d c , a d Pd–C b d d a c a 2.13 a d 2.17 Å, c . T b d −1.66 V, c a a a H_2.

F 1-b , ab ad c fi a a C=C d b b d a ac d Pd a . I ad (−1.72 V) a a 1,3-b ad . F b a , a d, c d ac a Pd a a a a b d −0.56 V. F a ad a , Pd a b d b a ca b a a d c a .

Reaction mechanism of 1,3-butadiene hydrogenation

T d a ac a c -ad H_2 a d 1,3-b ad Pd SAC (IS1 F . 3). I c -ad a , b d H_2 a d 1,3-b a- d −0.21 V a d −1.09 V, c . F c c d c , ab ca b a 1,3-b ad a 1, 2, 3, a d 4. A d ca d Sc 1, b c ad b d d a a ac a (C$_1$) (C$_2$) ca b C$_1$=C$_2$ d b b d ad b d Pd, 2-b -1- ad ca (2B1R) a d 1-b -1- ad ca (1B4R), c . A F . 3, ca c a- d ca a add H C$_2$ a fi- ca a ba 1.89 V a ac 0.50 V, a ac H C$_1$ ba c (1.33 V) a d ac b c - a . A a , a c d d a a d c a a d d . I a a (TS1) a a ac a a (IS1 → TS1 → IM1), d a c C$_1$–H b d 1.46 Å a d H–Pd b d 1.65 Å. Aft ac , d a (IM1 2B1R*) ad b a Pd c a -d a c fi a a C–Pd d a c 2.09 Å.

T fi d a a SAC ca a d ac . I ba 1.33 V a a Pd ca a d d a ac , c 1.24 V Pd(111).[14] T c a c (0.35 $^{-1}$)[12] SAC a a d Pd a c a a c ab 4 (>6.5 $^{-1}$).[43]

T fi d a d c b d ab Pd a a ad H_2, b ca c - -π-ad 13BD* a -π-ad - 2B1R* acc a d b a Pd-b d H. T a b a d a c a a a H_2 (4.7%),[12] a d c a a fi a d c . T ad a add a H_2 a a b d −0.20 V H–H b d 0.81 Å, a ab . I F . 4, fi c d d a a IS2. T a ac C$_2$ 2B1R* b Pd-b d H ad a a ba 0.35 V. A a a (TS2), H–Pd d a c 1.57 Å H–C$_2$ d a c 1.59 Å.

T b c c d d a
a a . O a d, 1-b
d c ca c Pd, a F . 4, a -
π-ad $C_3{=}C_4$ (ad
−1.72 V). I F . S3,† a c c
a a (TS2) a d ad b d 1-b (1B*) a d
c a a fica a -
c . T ca a d a c d d
d a b a , c
a b a . O a d, 1-b
d c ca d b, ad a d c a a
−0.65 V, a a fi . I
d ac , d d a , b d
b c a b d c-
a d 1-b , a b d a
$C_3{=}C_4$ d b b d d b ad ca a d b a Pd
SAC.

Post-transition-state dynamics

B c TS2 F . 4, d ffic a
$C_3{=}C_4$ a Pd a d c 1-b
c d d d d b, a a IRC a d
ad b d 1B* F . S3.† T d c
d c a , fi d a AIMD ca c a-
a TS2 (F . 5a) a c a
a . T fi a (2) a a c
F . 5b, c a 1-b d c a
d ab 15 Å a a Pd. T
a c ca b d SI. T c fi fi d ,
add a a c a d a a TS2
, b a d a d a c a d 16
- a d a c d a
ac b a d ff d ac d a
a d a ac c d a . A
a c ad d 1-b ,
- ad 1-b Pd SAC.

a c[25–30] a d a c ac ,[31] a -
a b d c SAC-ca a d ac .
I , c a c da a
d ff a P (111) a d Pd(111), d ff
ad 1,3-b ad a d 1-b c b -
a d ff ab a ad ca
d a a b c d c 1-
b .[14] T , d a c d d a a
c .

Conclusions

I , add a
d a a c d a 1,3-b ad
ca a d b a Pd SAC a c d a . F , DFT
ca c a d c da a SAC ac
a d ca a c c a . O Pd SAC d
c a c a a . F
c a ca H –P a c a , d a
1,3-b ad 1-b d a a
c d a d add $C_1{=}C_2$
d b b d Pd-ad b d 1,3-b ad b Pd ac a d
H_2. P a a , d a ca d 1-b
d aft c d d a a d -
ad d c Pd a d b
b d a d a d a . T ca
c d d ca a a d d c
a c d a c . T c a c
a b a SAC c a d ff a ff c-
d c SAC ca a d c -
ca a a .

Conflicts of interest

T a c fl c d c a .

Acknowledgements

W ac d Na a Na a Sc c F -
da C a (21673040 S. L.), Na a Sc c F da
F a P c (2016J01052 S. L.), F U
Q a Sc a P a (XRC-17055 S. L.), a d U.S.
Na a Sc c F da (CHE-1462109 H. G.). L. Z.
ac d a a C Sc a
C c (201604890009).

Notes and references

1 M. L. D , *Stud. Surf. Sci. Catal.*, d. L. C , E , 1986, . 27, . 613–666.
2 T. O c a b, J. Ma a d a d A. R , *J. Catal.*, 1989, **119**, 517–520.
3 A. Sa a , Z. Z d , G. S fl , J. W. H a d L. G c , *J. Catal.*, 1995, **157**, 179–189.
4 J. G , M. A. V , C. E. G a a d R. T d , *J. Catal.*, 2001, **199**, 338–345.

K. N. H , *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, E848–E855.
32 G. K a d J. F , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
33 G. K a d J. F , *Comput. Mater. Sci.*, 1996, **6**, 15–50.
34 J. P. P d , K. B a d M. E , *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
35 P. E. B c , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
36 S. G , J. A , S. E c a d H. K , *J. Chem. Phys.*, 2010, **132**, 154104.
37 H. J. M a d J. D. Pac , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1976, **13**, 5188–5192.
38 G. H a , B. P. Ub a a d H. J , *J. Chem. Phys.*, 2000, **113**, 9901–9904.
39 G. H a a d H. J , *J. Chem. Phys.*, 2000, **113**, 9978–9985.
40 S. C a a a d D. L. B , *J. Chem. Phys.*, 1975, **62**, 2890–2899.
41 W. L. Ha a d D. G. B c , *Chem. Phys. Lett.*, 1980, **74**, 284–287.
42 Z. Ya , Z. L , G. L a d K. H a , *Phys. Lett. A*, 2007, **369**, 132–139.
43 G. Ga c a C a , F. J. Cad Sa A a d J. C. B , *J. Catal.*, 2003, **214**, 26–32.

