Hydrogenation: Basics and Examples

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Berlin 29.01.10.

What is hydrogenation?

$$CH_3CH_3 + H_2 \rightarrow 2\ CH_4$$

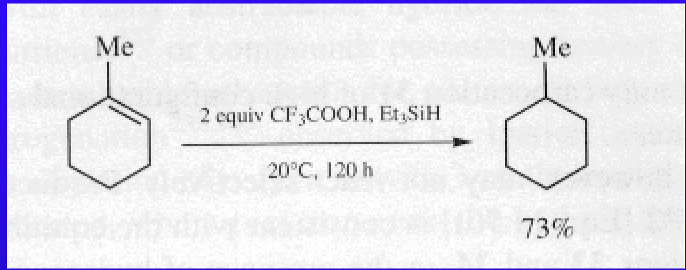
$$\boxed{CH_2CH_2 + H_2 \rightarrow CH_3CH_3}$$

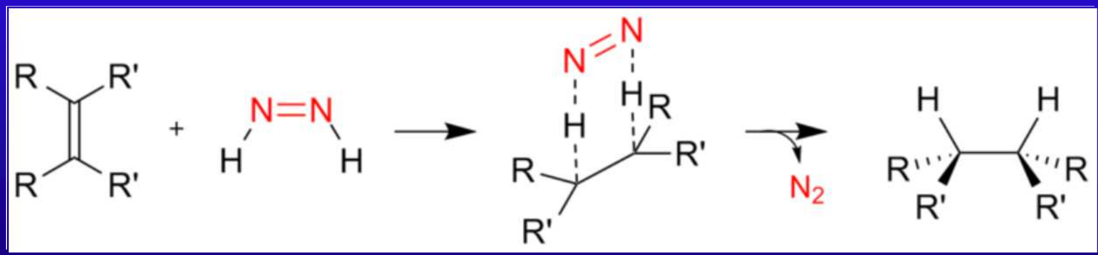
$$c\text{-}C_5H_{10} + H_2 \rightarrow C_5H_{12}$$

$$CD_2CD_2 + H_2 \rightarrow CD_2CDH + HD$$

Possible ways of hydrogenation?

- Heterogeneous catalytic: over metals
- Heterogeneous catalytic: over non-metals
- Homogeneous catalytic: metal complexes
- Chemical reduction: with diimide, $LiAlH_4$
- “Ionic hydrogenation”: with protic acid and hydride ion donor



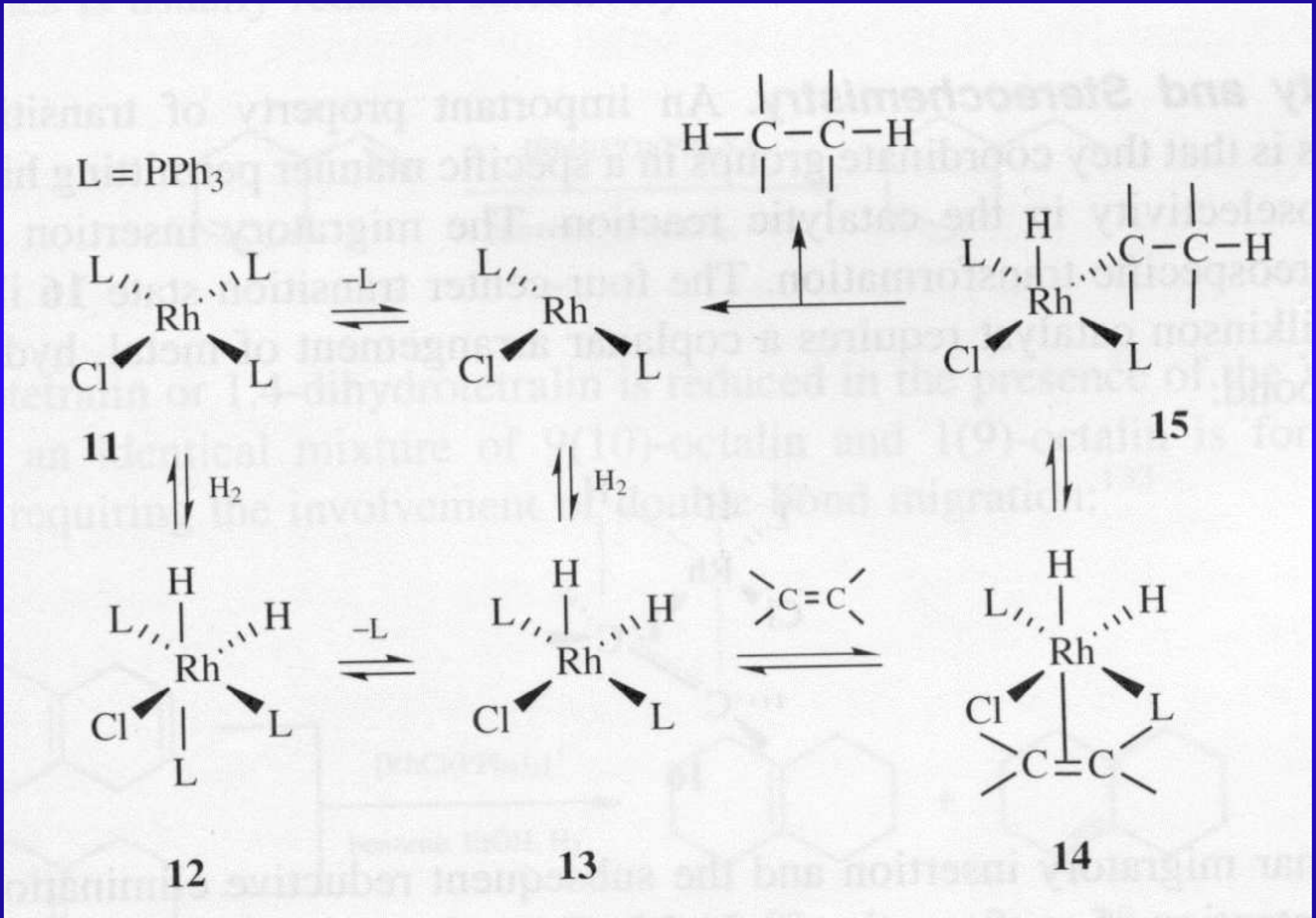


Application

- Petrochemical applications
- Food industry
- Pharmaceutical industry
- Chemical synthesis

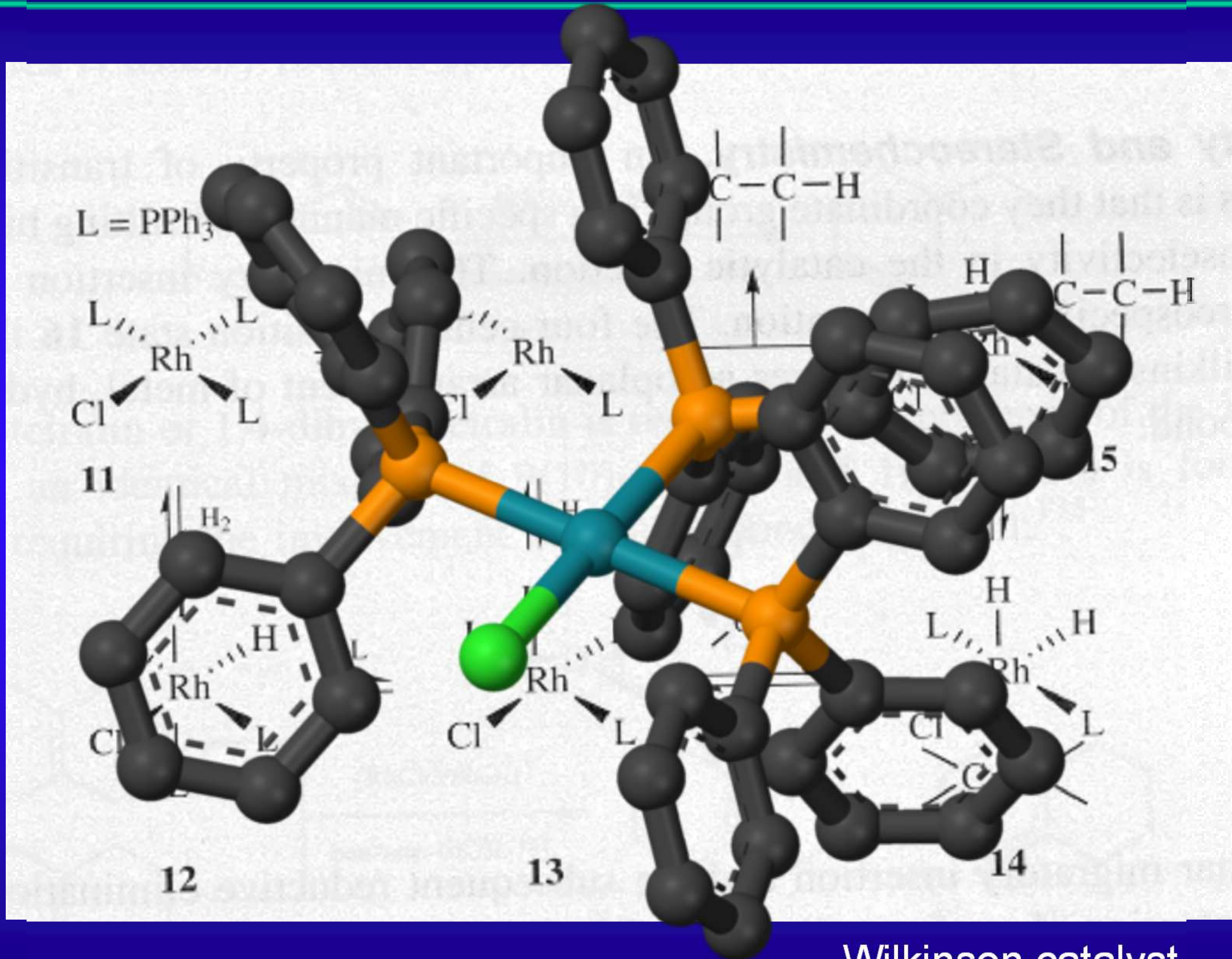
Industry	Molecular weight of product/g mol^{-1}	Synthetic steps to product	Production/t a^{-1}	kg by-product per kg product
Base chemicals	<50	1–2	10^6–10^8	<0.1
Bulk chemicals	50–100	1–5	10^4–10^6	<1–5
Fine chemicals	100–300	5–10	10^2–10^4	5–>50
Pharmaceuticals	100–1000	>10	10^0–10^3	25–>100

A homogeneous mechanism



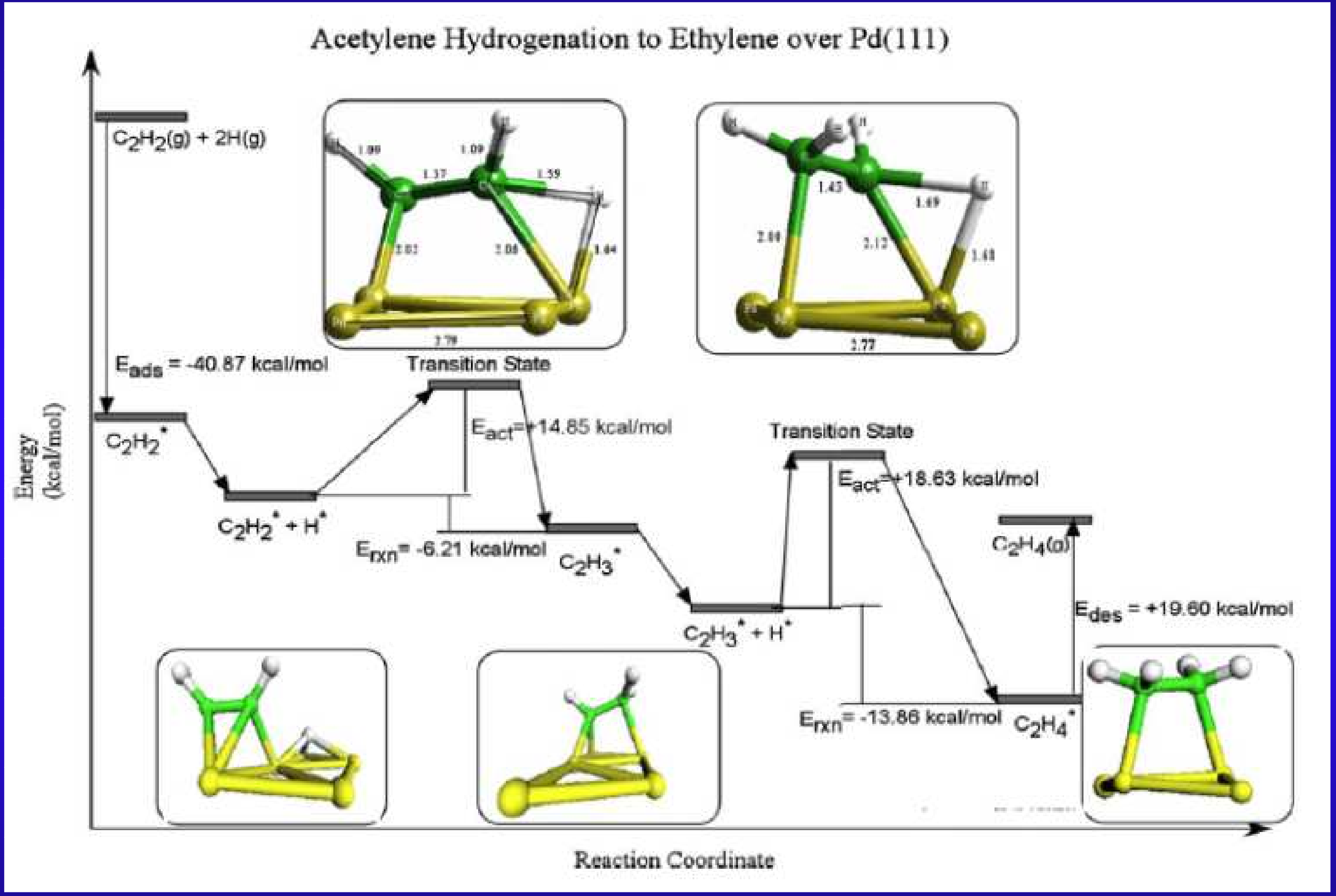
Wilkinson catalyst

A homogeneous mechanism



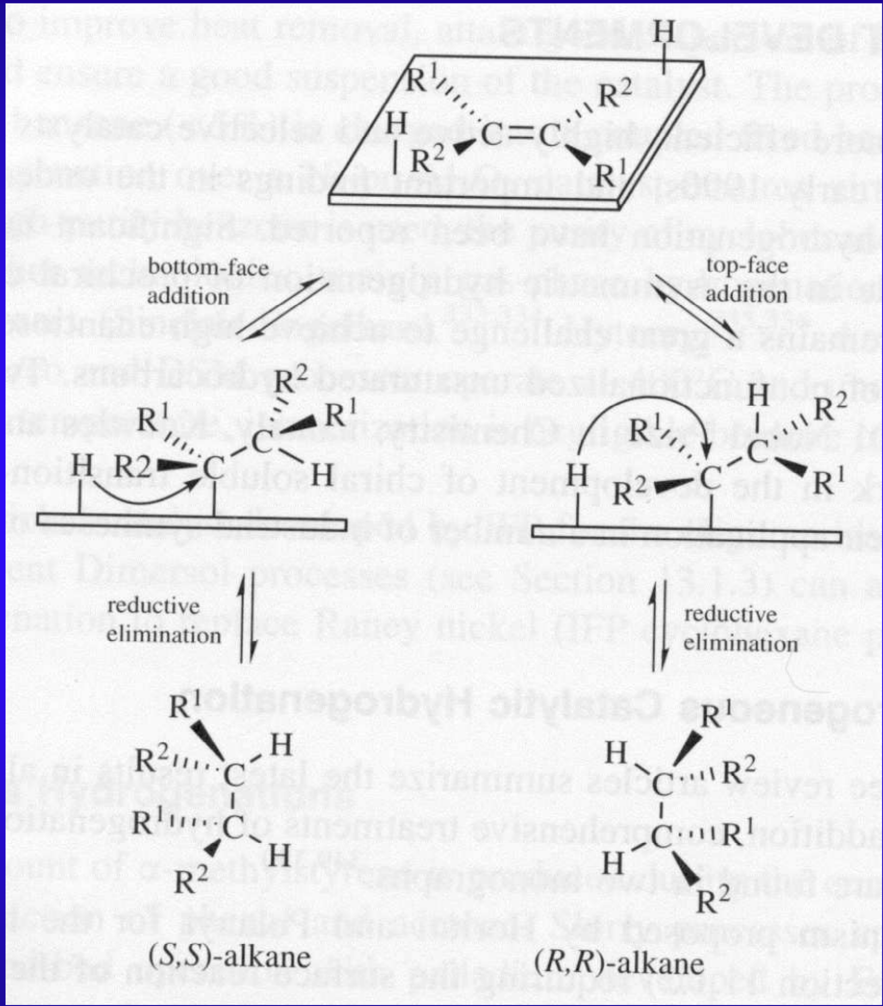
Wilkinson catalyst

Basics: L.-H.; H.-P.;



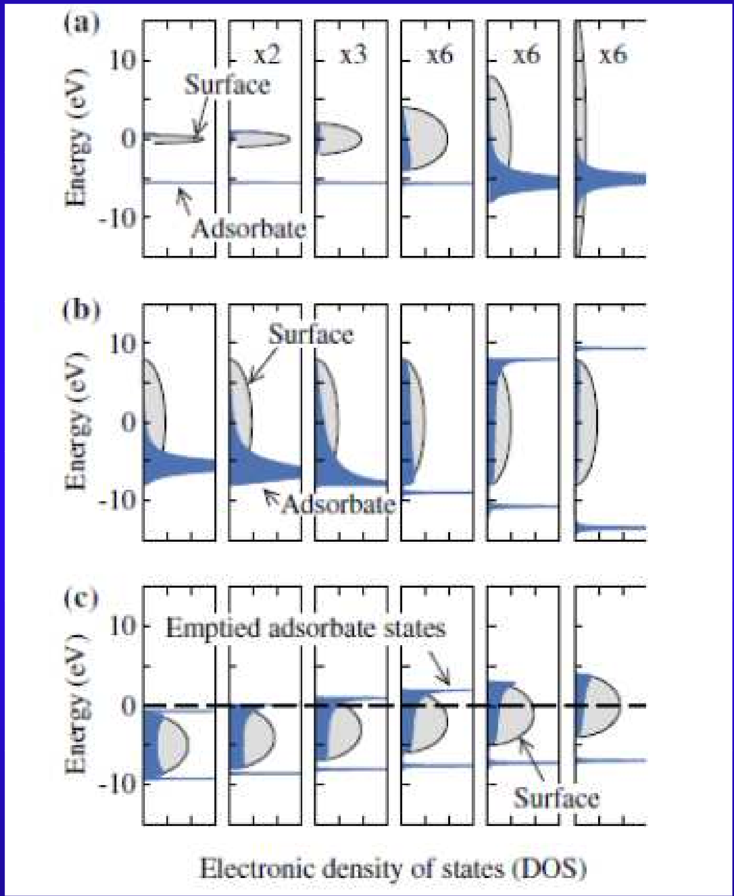
Neurock et al.: Journal of Catalysis 242 (2006) 1–15.

Basics: Syn stereochemistry



Both H adds from the same face of the functional group

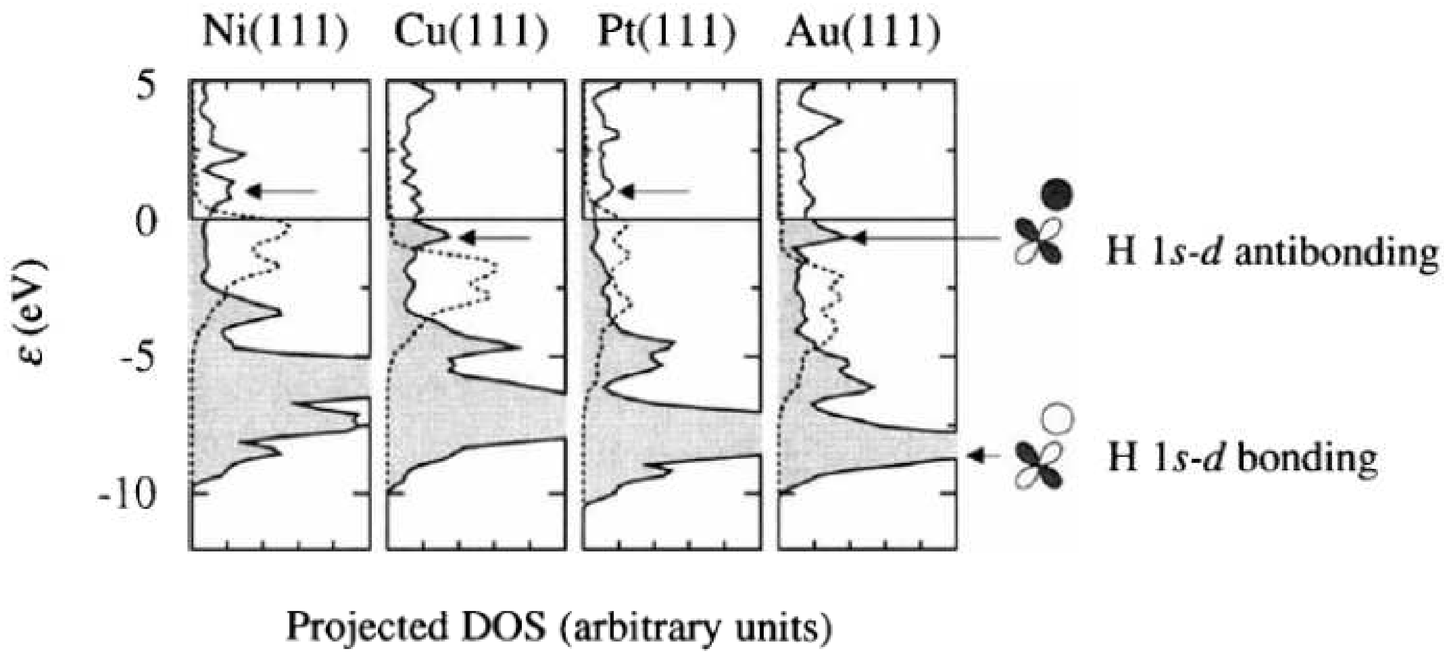
Basics: Adsorption



Newns–Anderson model of interaction in an adsorption system with a semi-elliptic DOS band (gray) at the surface and a deltafunction DOS on the adsorbate before the interaction. The resulting adsorbate state projected DOS (blue) takes a number of forms depending on the parameters.
(a) Increasing the bandwidth, (b) Increasing the interaction strength, (c) Increasing the energy splitting, |Ed-Ea|.

Hammer: Topics in Catalysis 37 (2006) 3.

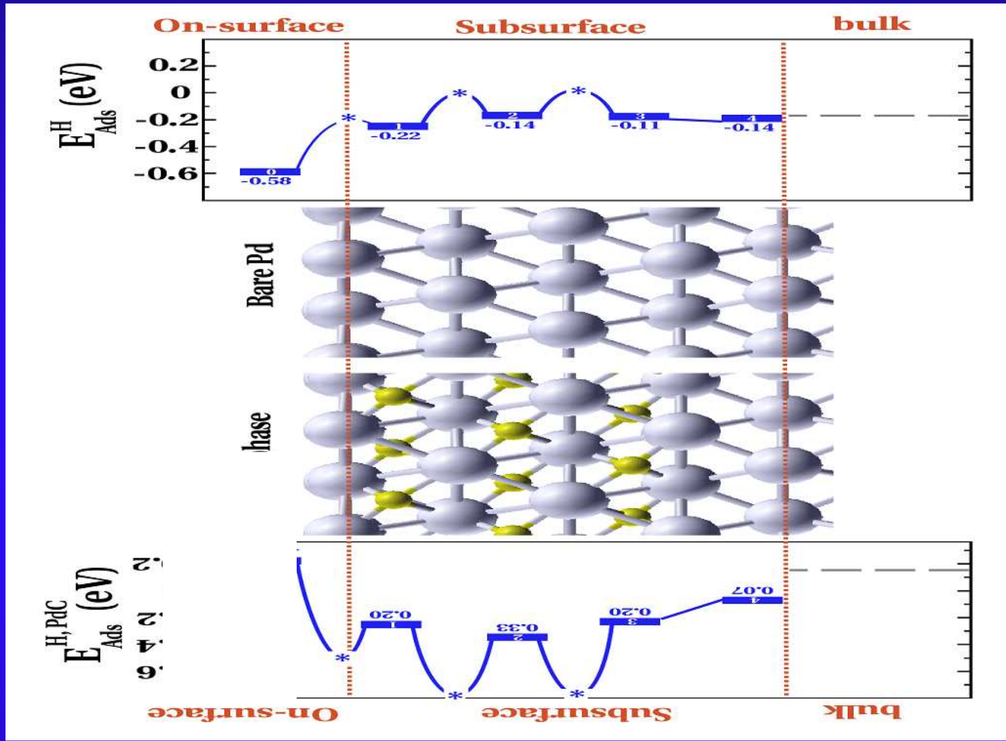
Basics: H-M



Hammer, Norskov: Nature 376 (1995) 238.

Additional complexity: particle size, low coordination sites, strain, etc.

Basics: H in Pd



Special character of surface/subsurface/bulk H:
- Adsorption energy
- Sticking probability
- Reactivity

Basics: What metals for which reaction?

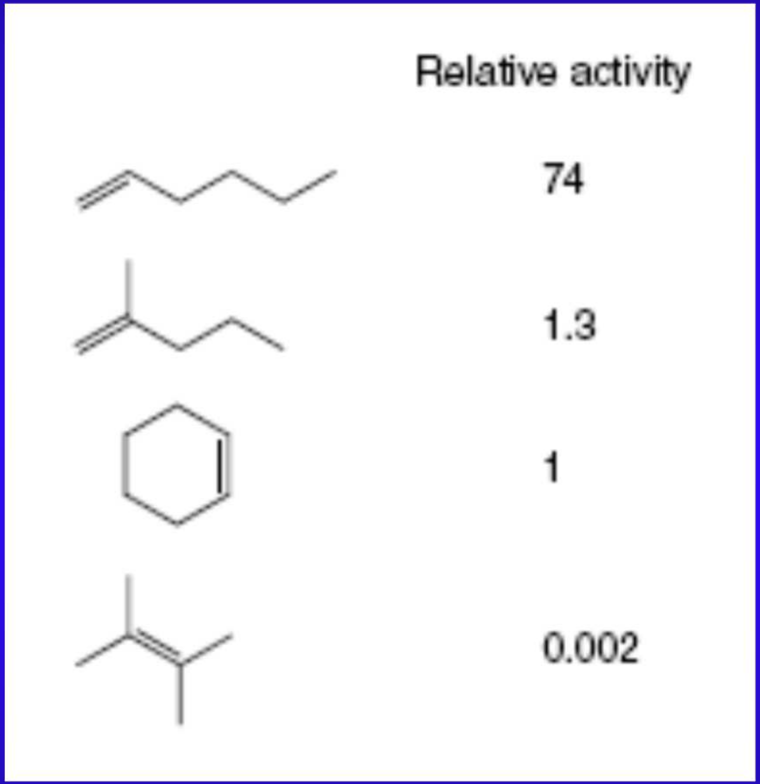
Chemoselectivity

Reaction	Catalyst	Reaction medium	p/bar	T/°C
$R_2C{=}CR_2 \rightarrow R_2CH{-}CHR_2$ (R = H, alkyl, aryl)	Pd, Pt, Ni	Slightly polar	3–100	5–100
$RC{\equiv}CR \rightarrow RCH{=}CHR$ (R = H, alkyl, aryl)	Pd	Slightly polar	1–3	5–50
$R_2CO \rightarrow R_2CHOH$ (R = alkyl)	Pt, Ni, Ru	Polar	1–10	50–150
$RCHO \rightarrow RCH_2OH$ (R = alkyl)	Pt, Ni, Ru	Polar	1–10	20–100
$ArCOR \rightarrow ArCH(OH)R$ (Ar = aryl, R = alkyl)	Pd, Ni, Pt	Slightly polar	1–10	5–50
$RCN \rightarrow RCH_2NH_2$ (R = alkyl, aryl)	Ni	Ammonia	20–40	20–100
	Pt, Pd	Polar + HCl	1–10	20–100
$RCH{=}NOH \rightarrow RCH_2NH_2$ (R = aryl, alkyl)	Ni, Pt, Pd, Rh	Acidic	1–50	5–100
$R_2C{=}NR \rightarrow R_2CHNHR$ (R = H, alkyl)	Pt, Ni	Polar	3–50	50–150
$RN_3 \rightarrow RNH_2$ (R = alkyl, aryl)	Pd	Polar	1–10	20–50
$RNO_2 \rightarrow RNH_2$ (R = aryl)	Pd, Pt, Ni	Various	1–5	5–50
$RX \rightarrow RH$ (R = aryl, X = Hal)	Pd	Basic	1–10	50–100
$RCH_2X \rightarrow RCH_3$ (R = aryl, X = Hal)	Pd	Basic	1–10	20–100
(R = aryl, X = O, N)	Pd	Acidic	1–10	20–100
$RCOX \rightarrow RCHO$ (R = alkyl, aryl, X = Hal)	Pd	Basic	1–10	20–50
$RCOOR \rightarrow RCH_2OH$ (R = alkyl, aryl)	Cu, Ru	Apolar	100–300	100–200
$Ar \rightarrow R$ (R = saturated ring)	Rh, Pt	Various	3–100	20–100
	Ru, Ni	Various	20–100	50–150
$HeteroAr \rightarrow R$ (R = saturated heterocycle)	Pt, Pd	Acidic	20–50	50–150
	Rh, Ru	Various	5–100	50–150

Handbook of Catalysis: p.3286.

Hydrogenation of functional groups

Basics: Sterical effects?



Hydrogenation rate:

- RCH=CH2 > RCH=CHR

- Cis > Trans

- Decreases with increasing substituents

Basics: sterical effect, isomerization

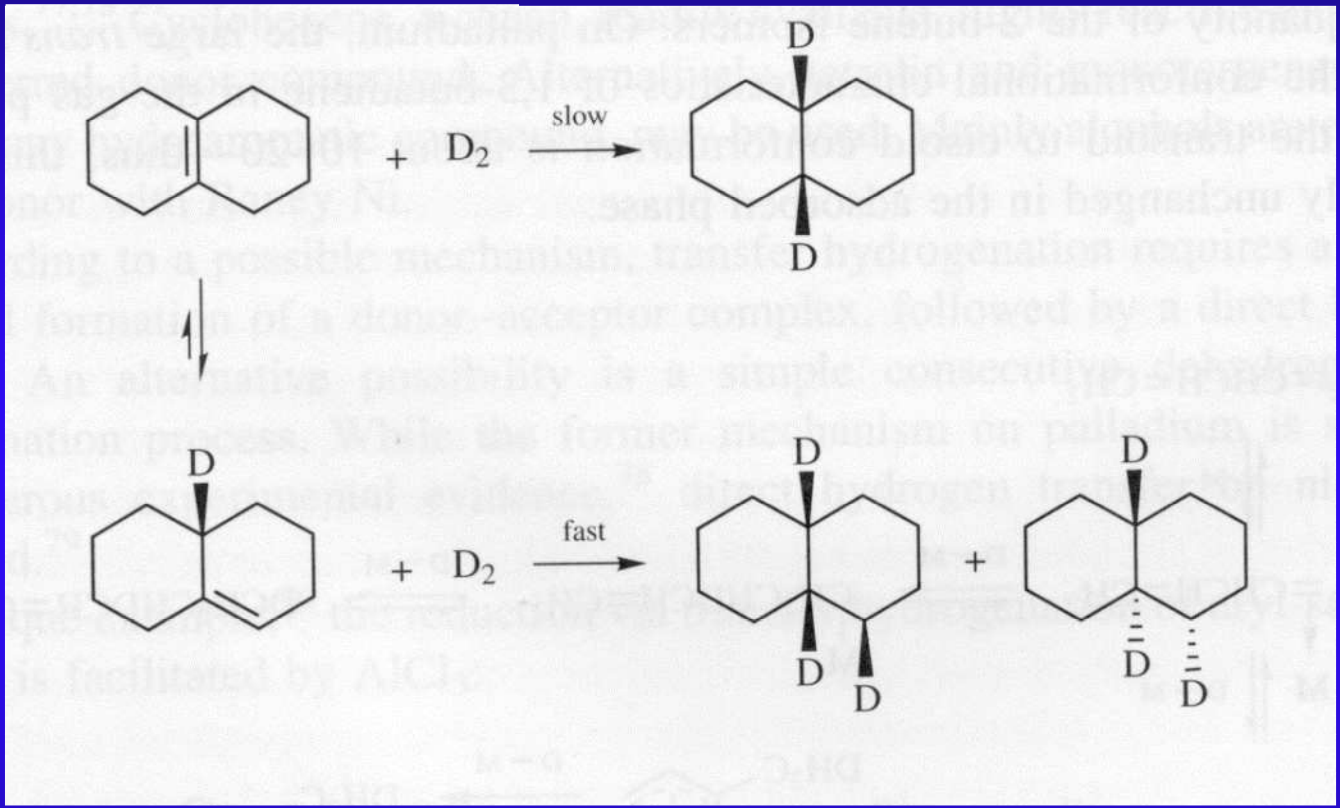
Hydrogenation of 1- and 2-pentyne at 320 K

Catalyst	Reactant, Products	% yield at reaction time (min)								
		0.5	5	10	20	35	45	55	75	95
Pd/SiO_2	1-Pentyne	99	83	67	43	20	12	5	5	5
	1-Pentene	1	17	33	56	72	79	79	73	66
	t-2-Pentene	0	0	0	0	0	0	4	6	8
	c-2-Pentene	0	0	0	0	0	0	0	0	0
	Pentane	0	0	0	1	8	10	12	17	20
Pd/SiO_2	2-Pentyne	91	39	10	1	0	0	0	0	0
	1-Pentene	0	0	1	2	2	2	2	2	2
	t-2-Pentene	0	0	0	10	20	25	29	36	40
	c-2-Pentene	5	44	80	81	70	62	57	47	40
	Pentane	0	1	2	5	9	11	12	15	17

Jackson et al.: RKCL 73 (2001) 77.

Equilibrium: ~ 80% t-2-ene, 18% c-2-ene, 2%: 1-ene

Question

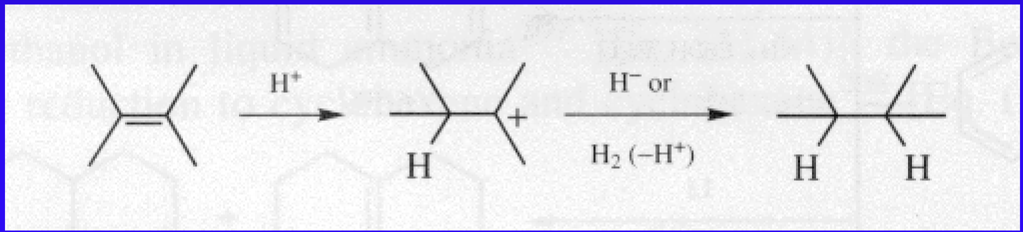


Pt catalyst

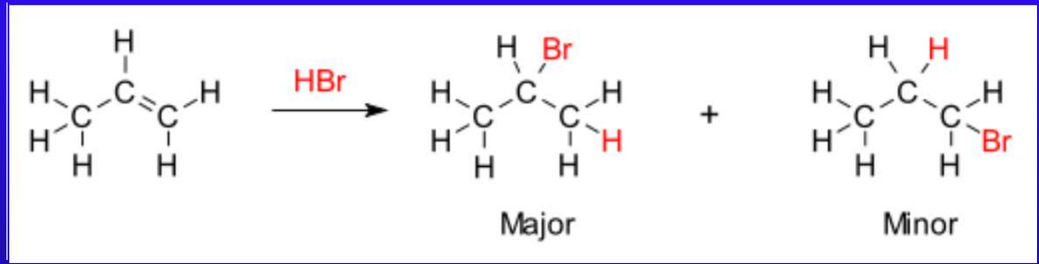
Question

Hydrogenation of tetra-substituted alkenes with relative ease?

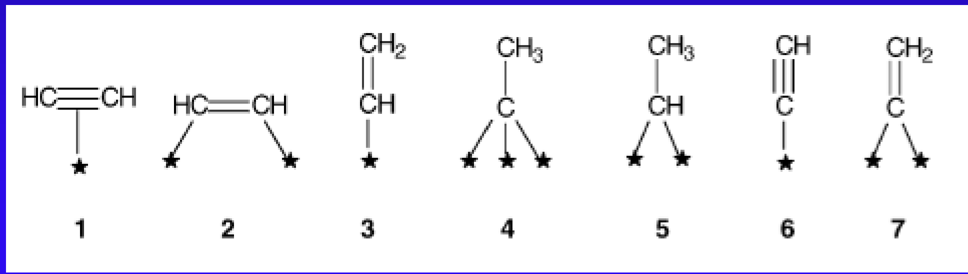
Tetra substituted alkenes readily undergo saturation in ionic hydrogenation



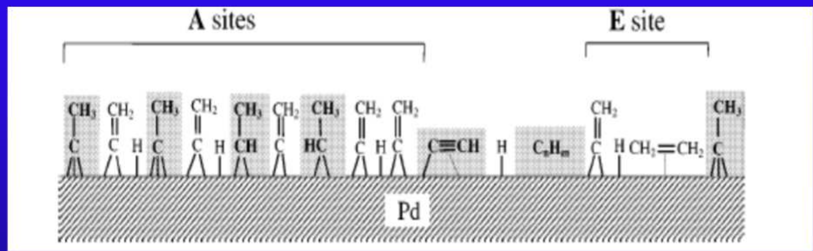
Why?



Basics: surface species

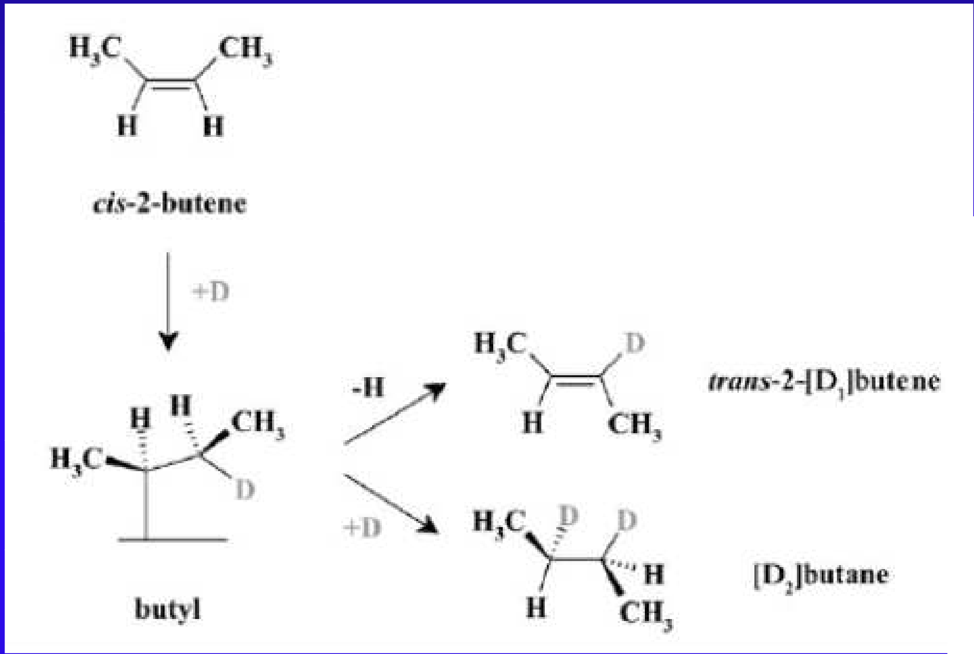


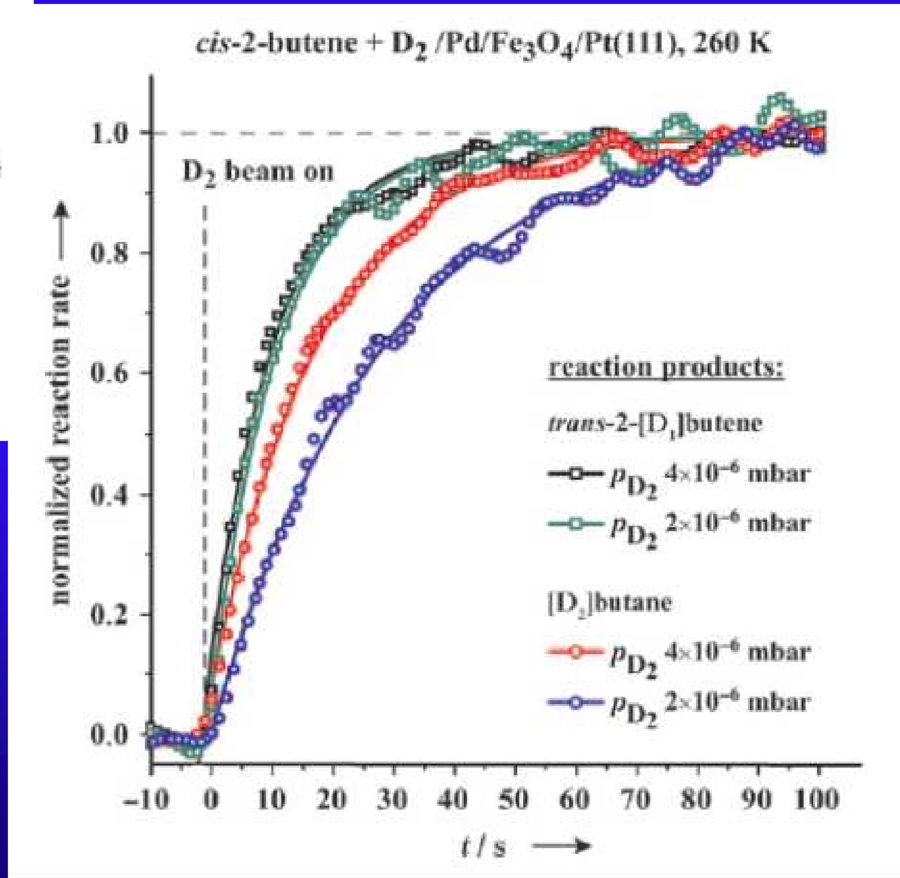
Proposed surface intermediates in hydrogenation of acetylene.



A. Borodzinski: hydrogenation between HC deposits

Example 1: subsurface H

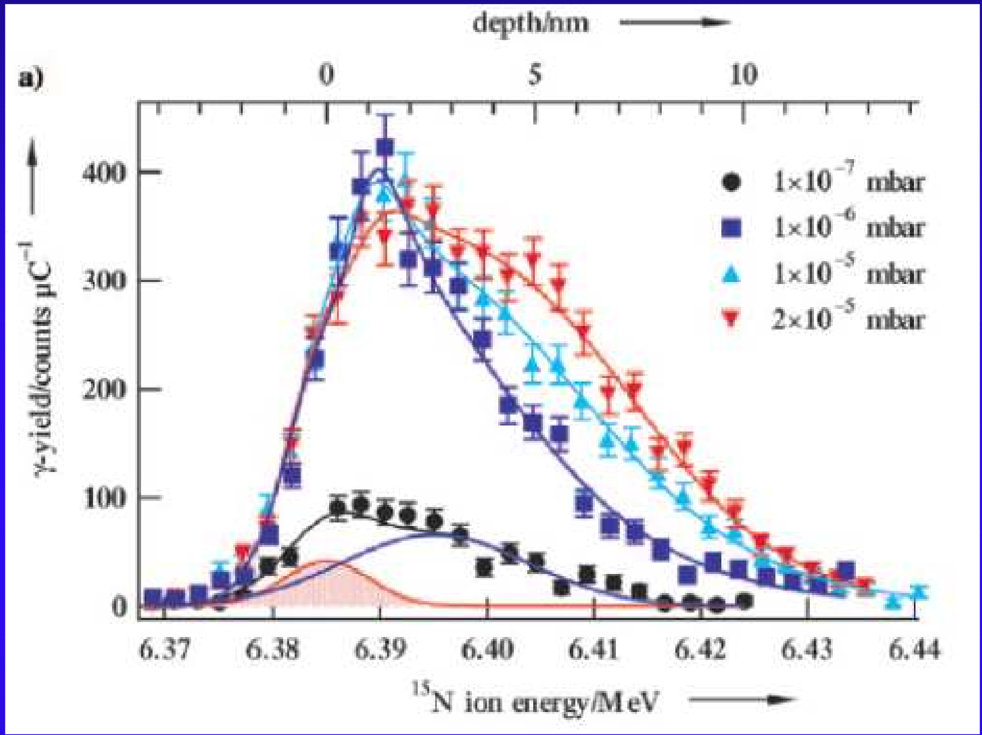


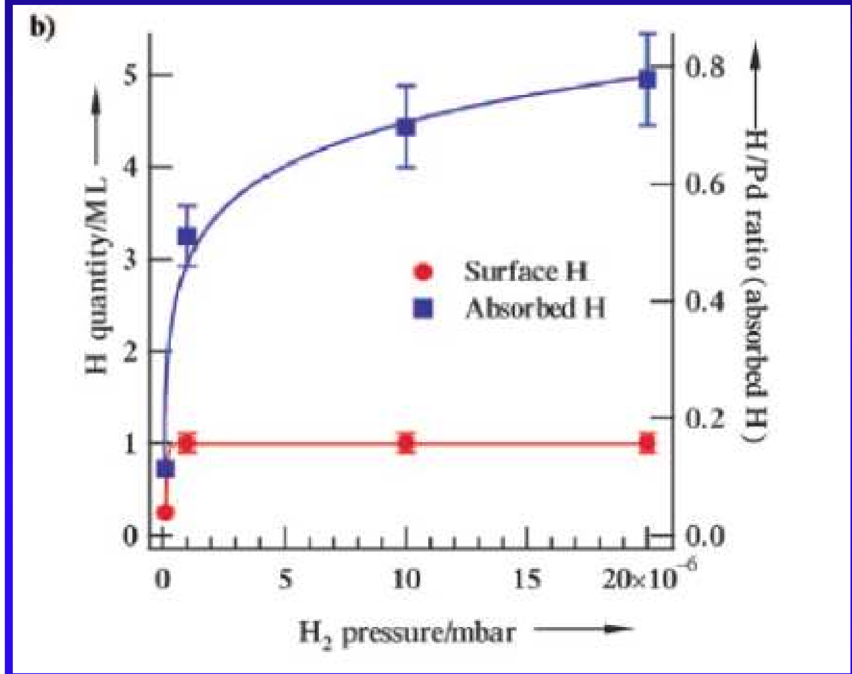


Different response to $p(D_2)$

Wilde et al.: Angew. Chem. Int. Ed. 47 (2008) 9289.

Example 1





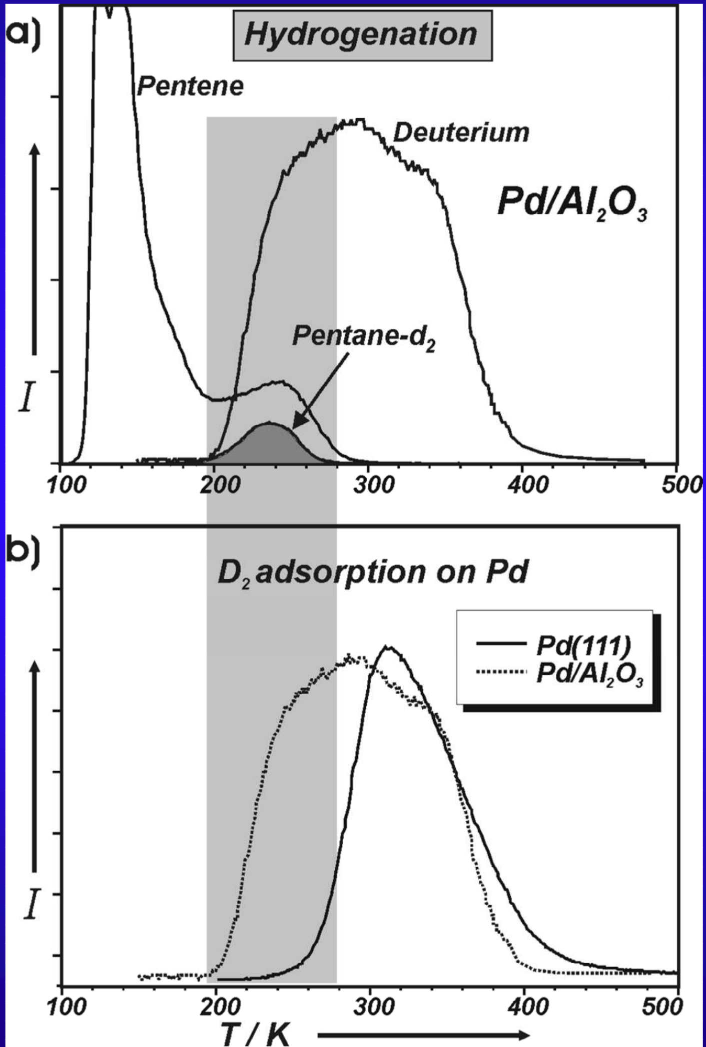
NRA: K. M. Horn and W. A. Lanford, Nucl. Instrum. Methods Phys. Res. B 29, (1988) 609.
M. Wilde, M. Matsumoto, K. Fukutani, and T. Aruga, Surf. Sci. 482-485, (2001) 346.

Surface H for isomerization

Subsurface H for hydrogenation

Wilde et al.: Angew. Chem. Int. Ed. 47 (2008) 9289.

Example 1



Pentenes to pentane

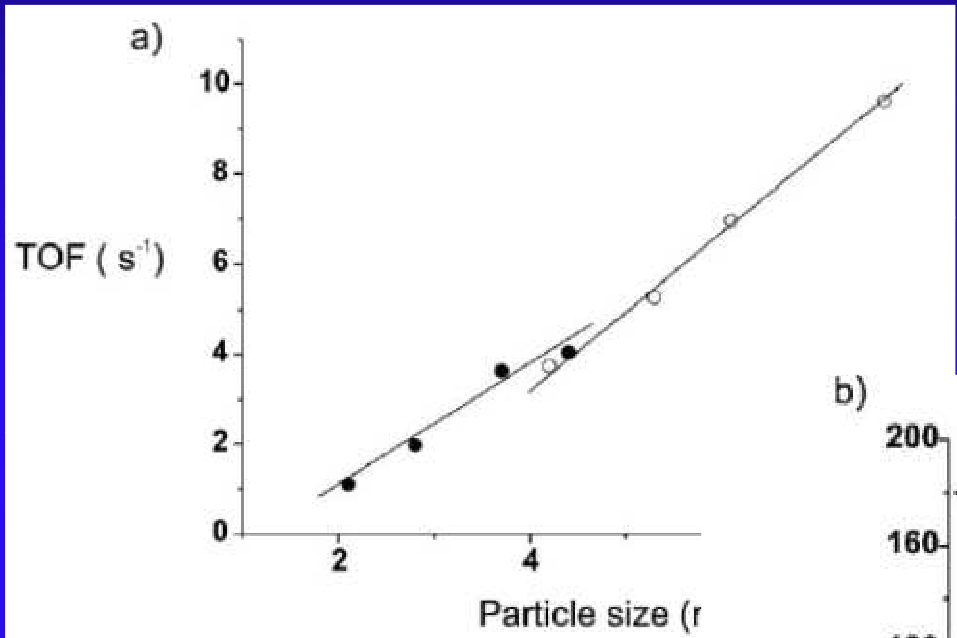
→ Hydrogenation in the presence of subsurface H [Pd particles]

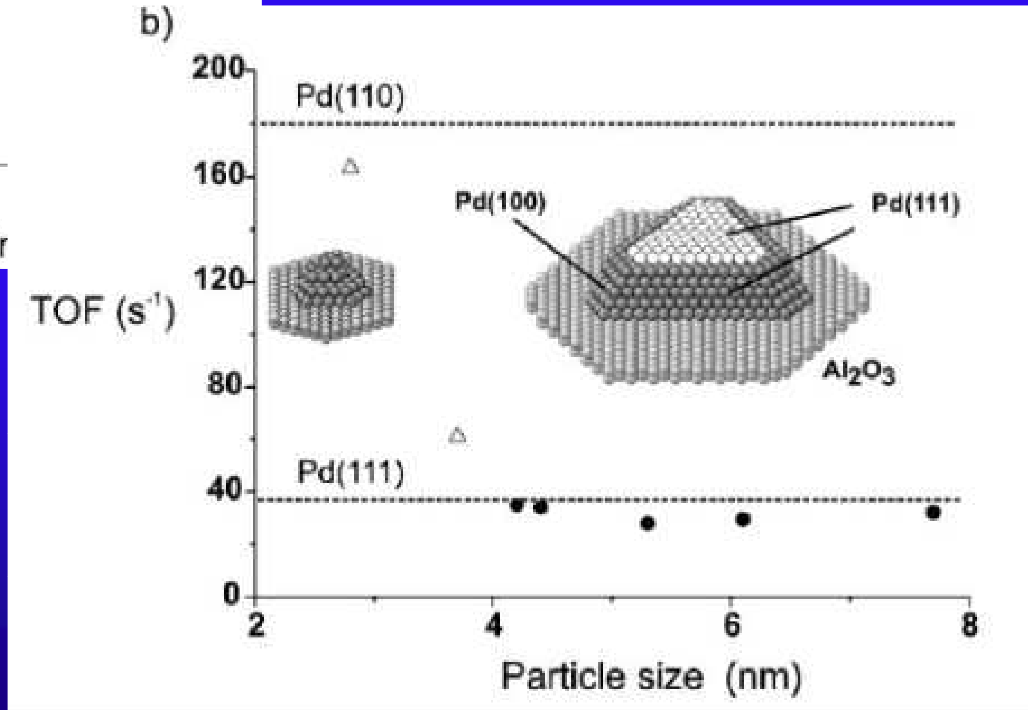
→ No hydrogenation without subsurface H [Pd(111)]

Doyle et al.: Angew. Chem. Int. Ed. 42 (2003) 5240.

Example 2: structure sensitivity

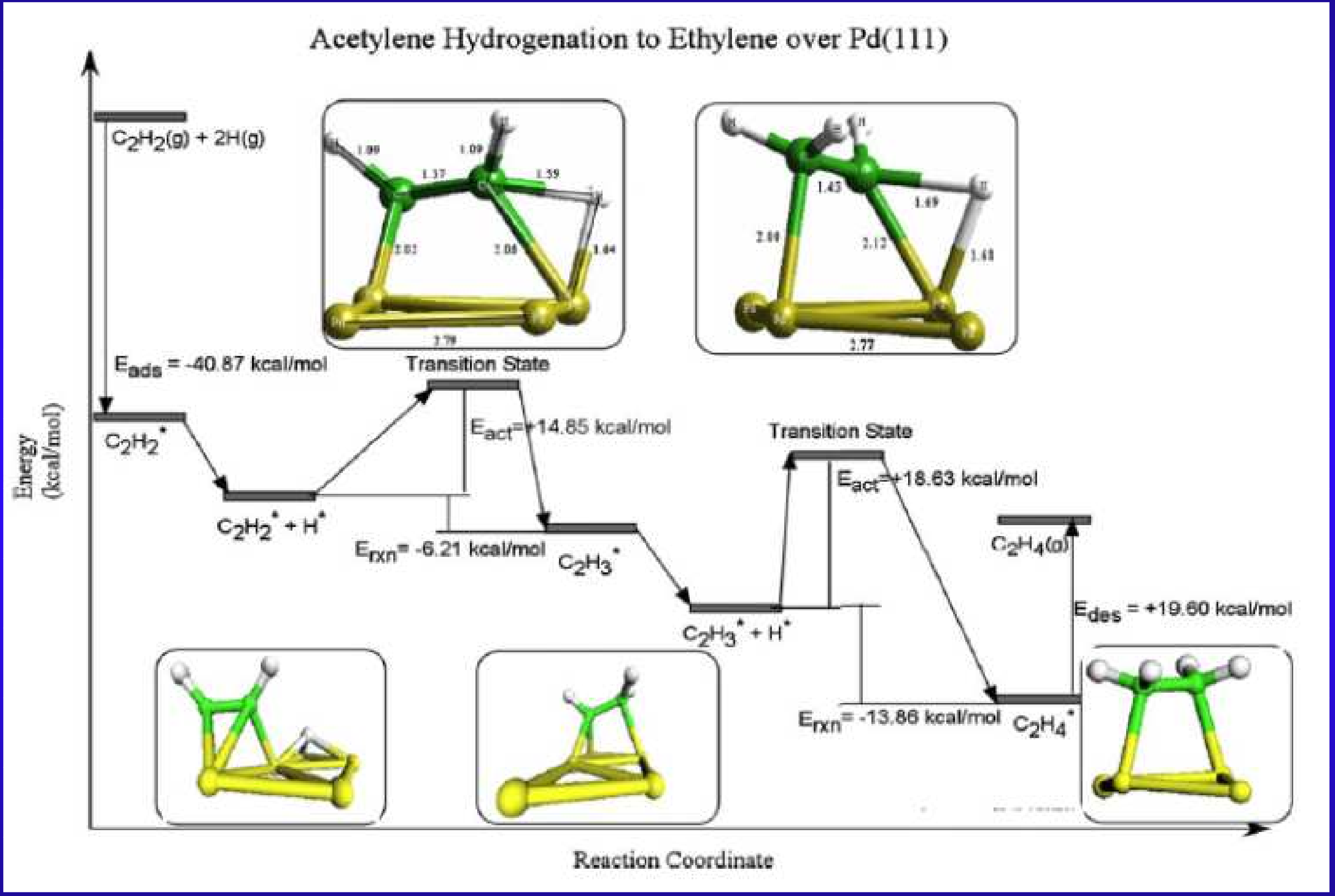
1,3-butadiene hydrogenation





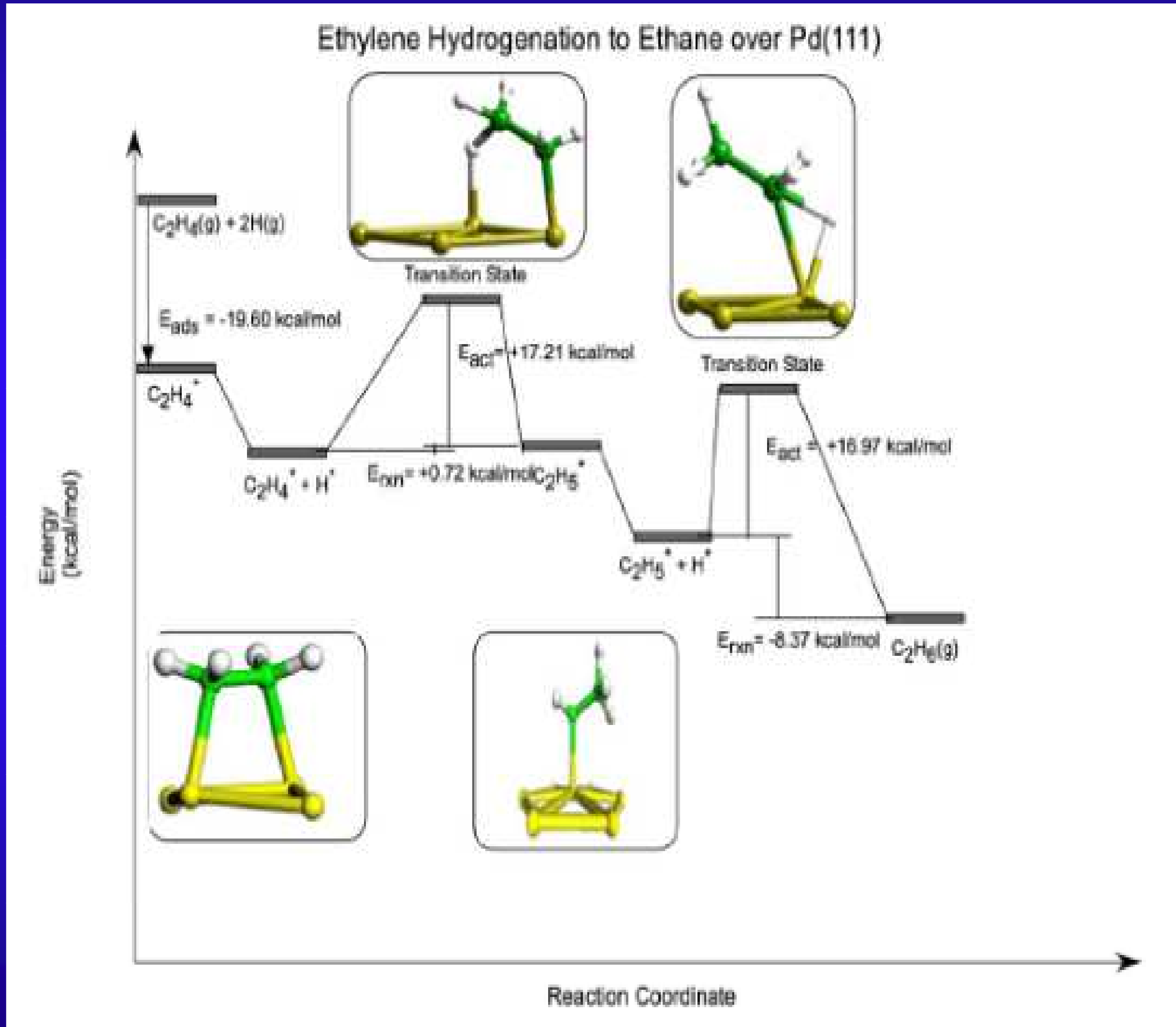
Rupprechter et al.: Chem. Comm. (2006) 80.

Example 3: 🕓 vs. 🖬 bond hydrogenation



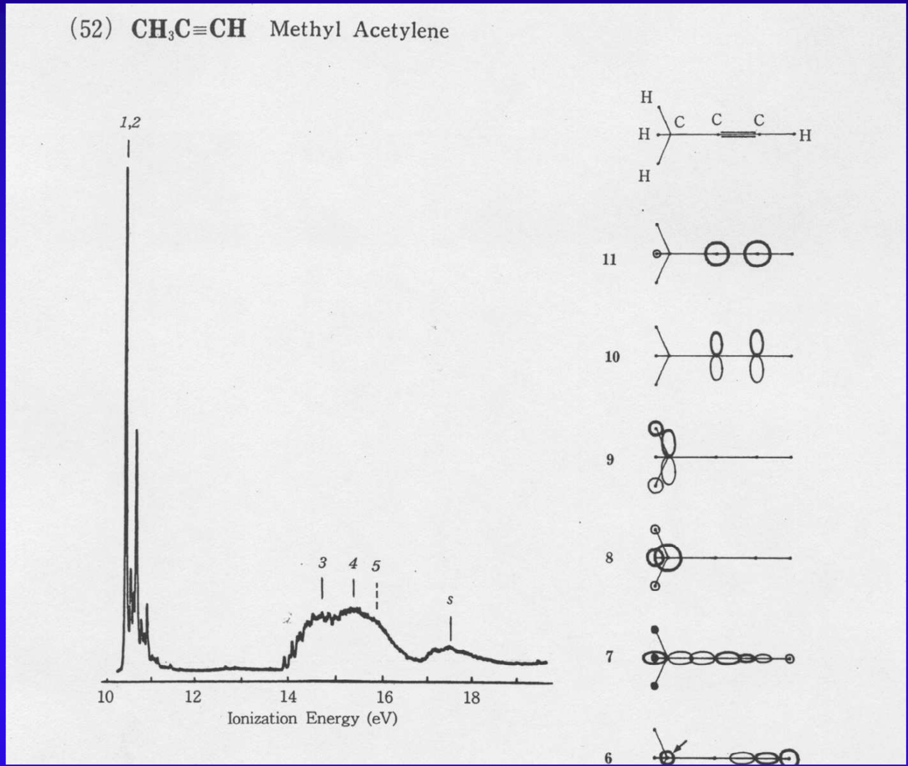
Neurock et al.: Journal of Catalysis 242 (2006) 1–15.

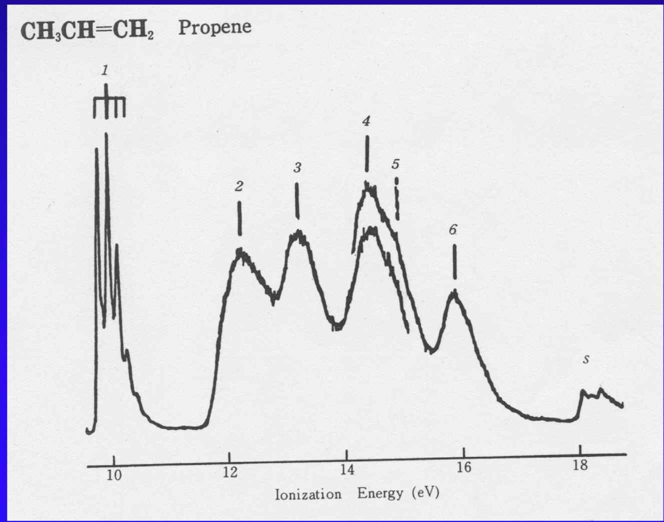
Example 3



Neurock et al.: Journal of Catalysis 242 (2006) 1–15.

Example 3





Kimura et al.:
Handbook of UPS spectra

For C_3H_4 the HOMO is situated ~0.4 eV lower than the corresponding level of C_3H_6: larger coupling with the metal *d* states, and thus to larger binding energy to metallic particles.

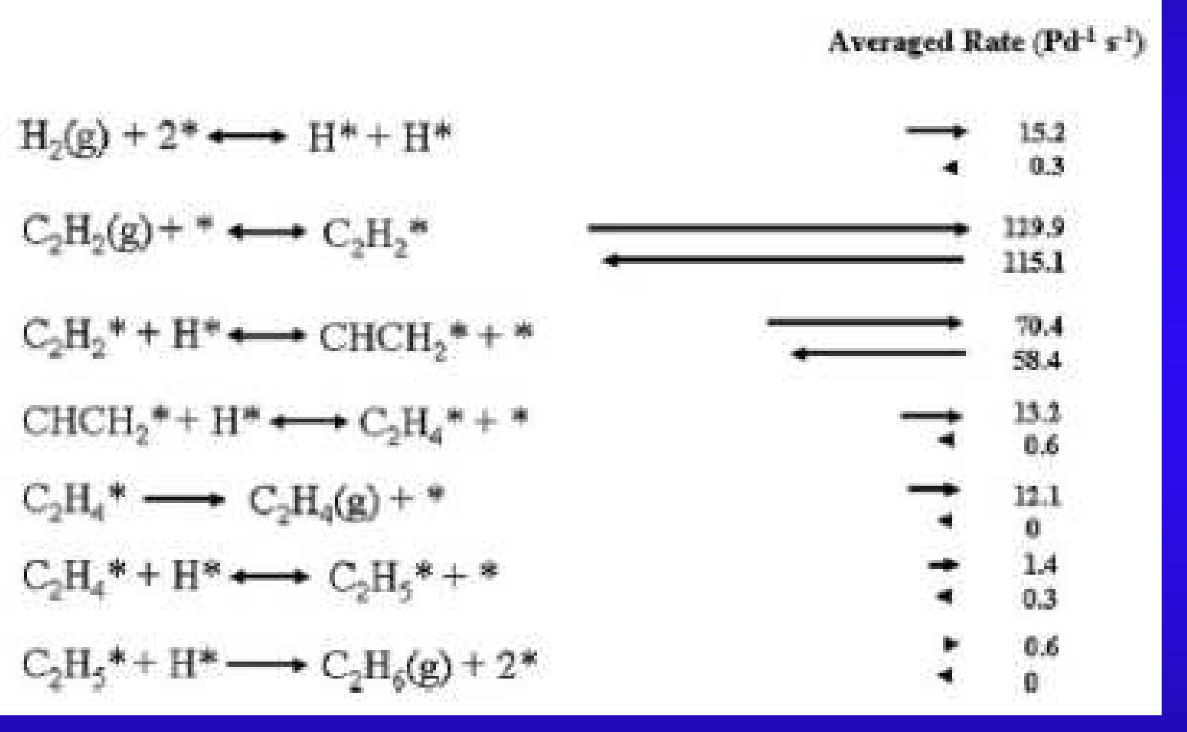
Example 3

	T (K)		
	300	325	350
Hydrogen	0.061	0.043	0.026
Acetylene	0.332	0.348	0.347
Vinyl	0.001	0.001	0.001
Ethylene	0.001	0.001	0.001
Ethyl	3.4×10^{-5}	2.1×10^{-5}	9.4×10^{-7}

Neurock et al.: Journal of Catalysis 242 (2006) 1–15.

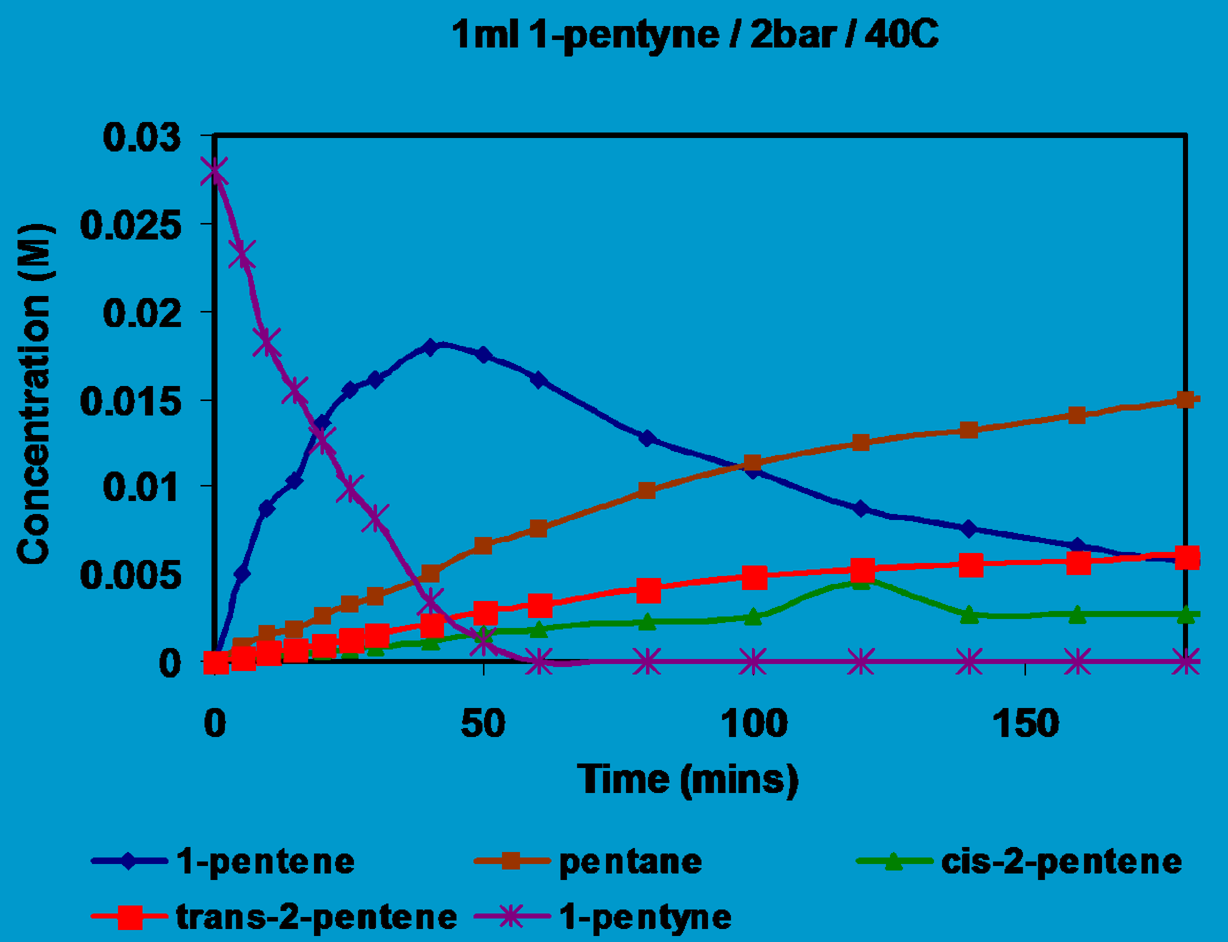
Simulated surface coverages of the reaction intermediates for acetylene hydrogenation over Pd(111) at PC_2H_2 = 100 Torr and PH_2 = 100 Torr

Example 3



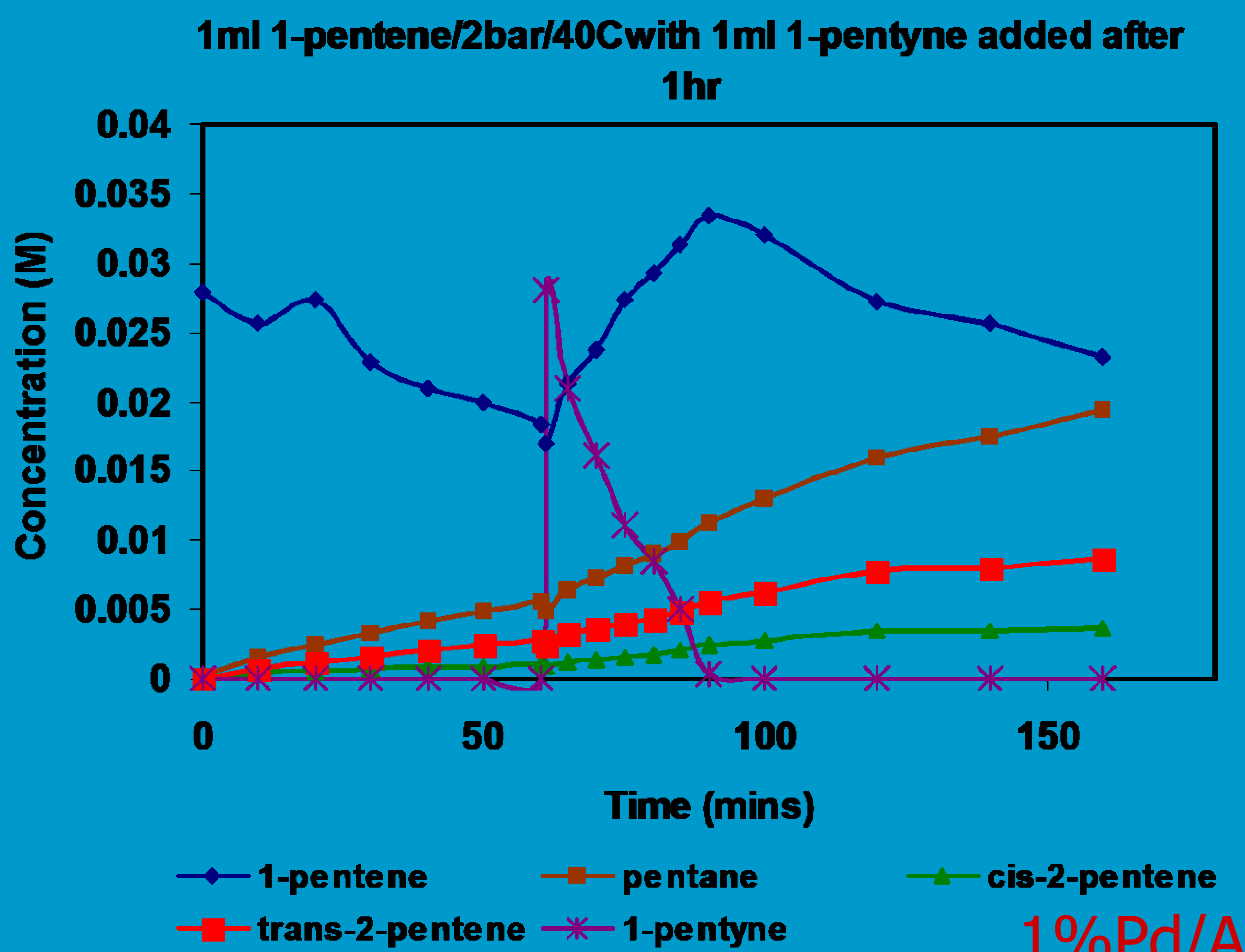
Neurock et al.: Journal of Catalysis 242 (2006) 1–15.

Example 3



1%Pd/Al_2O_3

Example 3



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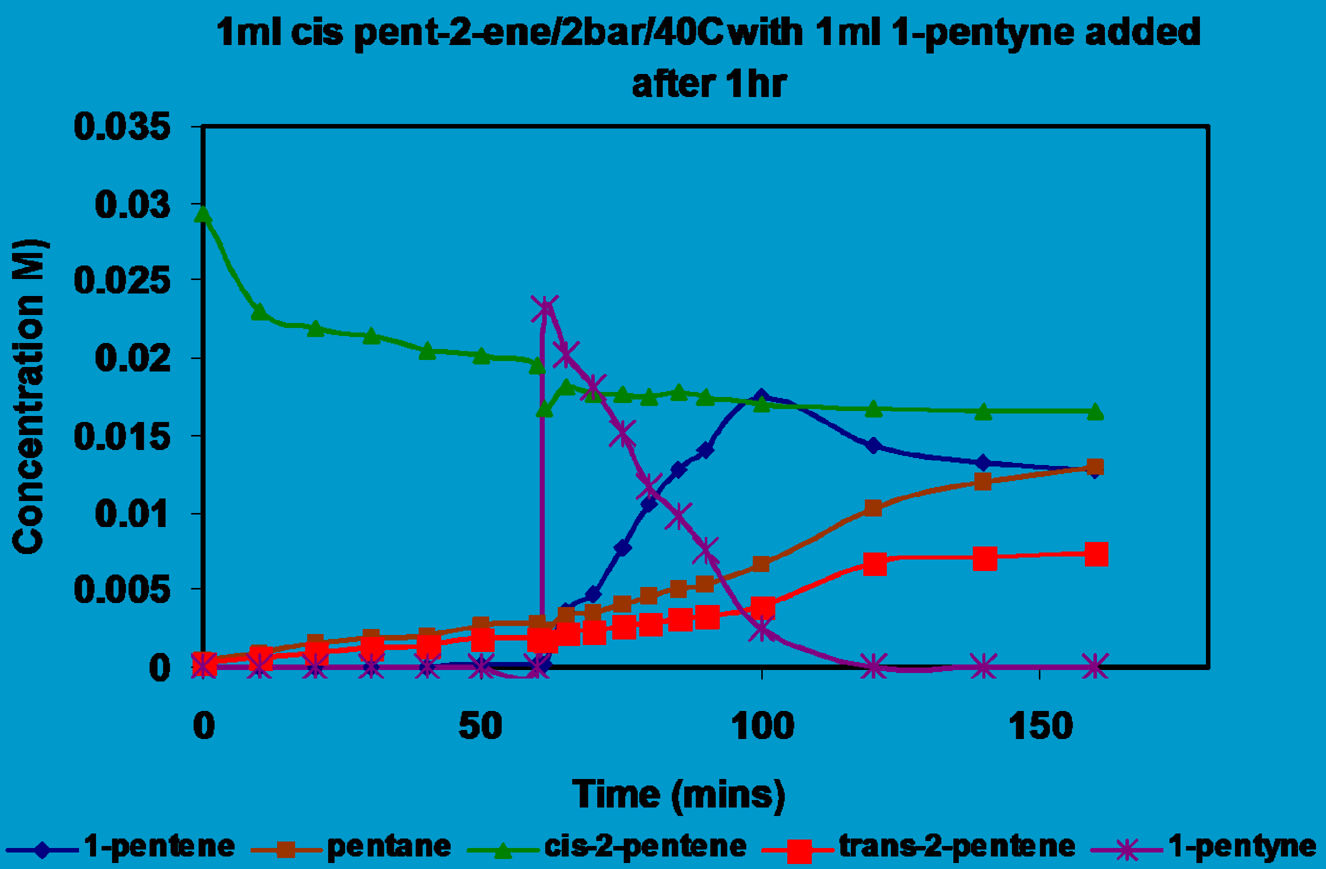
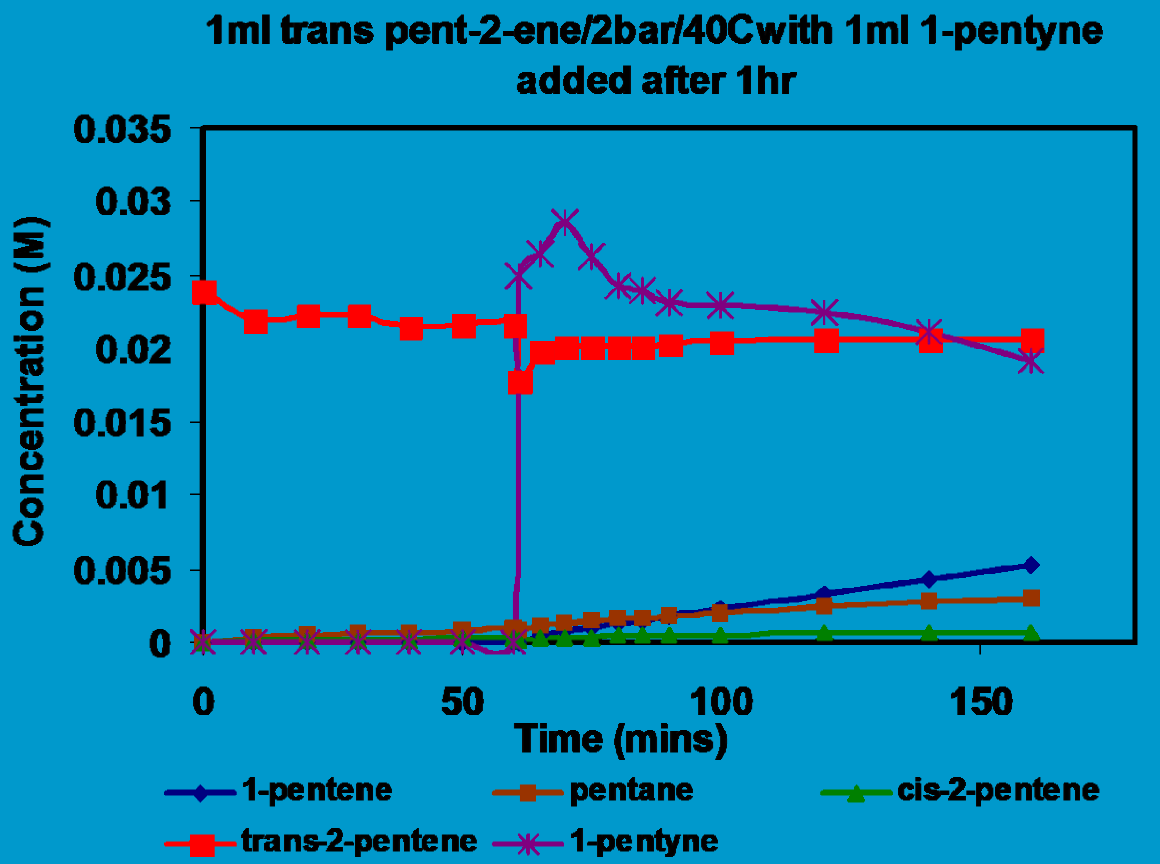


$1\%Pd/Al_2O_3$

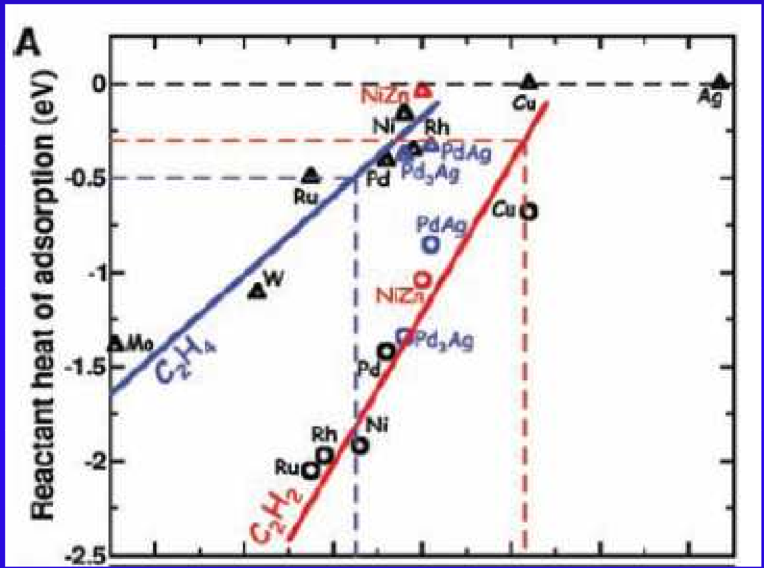
Example 3: effect of trans



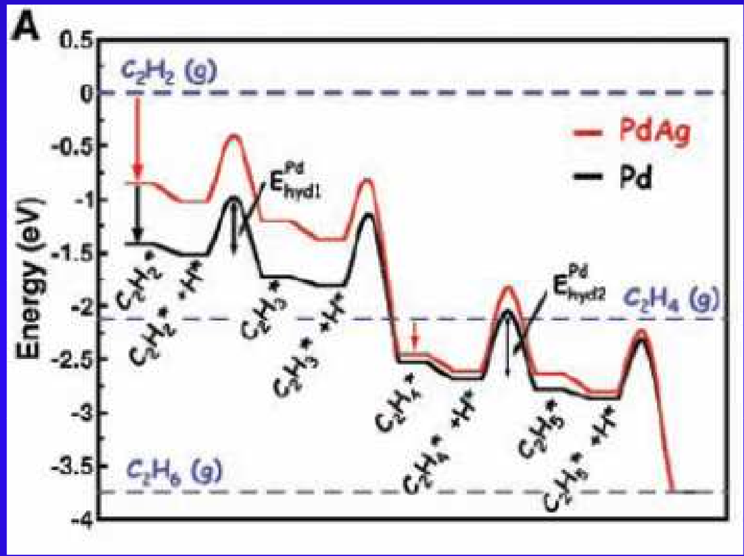
$1\%Pd/Al_2O_3$

Example 3

The heat of adsorption difference between alkyne and alkene can define selectivity.



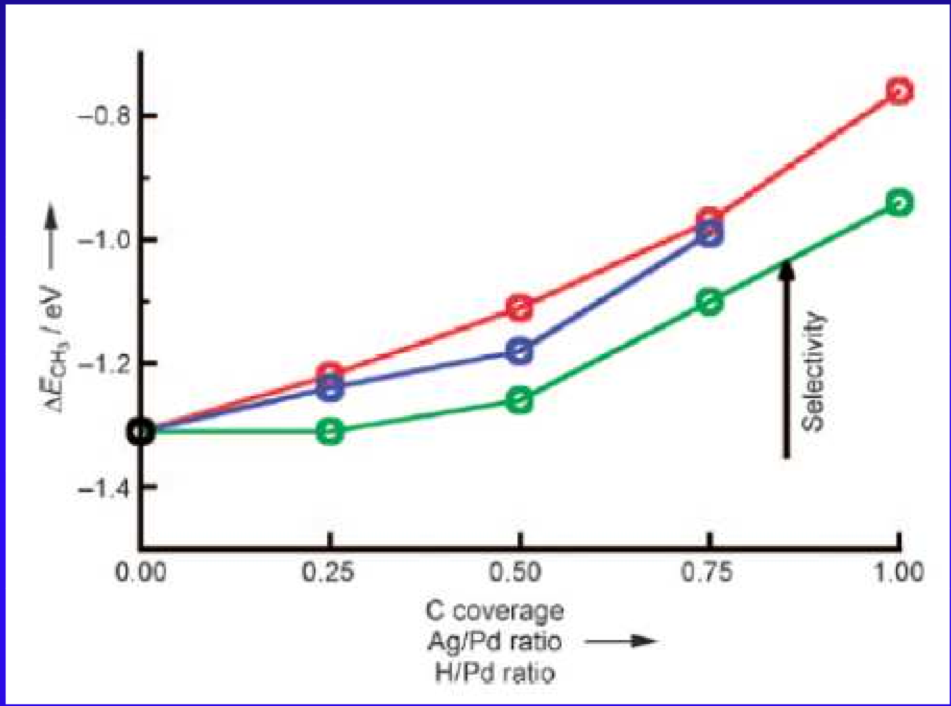
Methyl heat of adsorption



Reaction coordinate

Norskov et al.: Science 320 (2008) 1320.

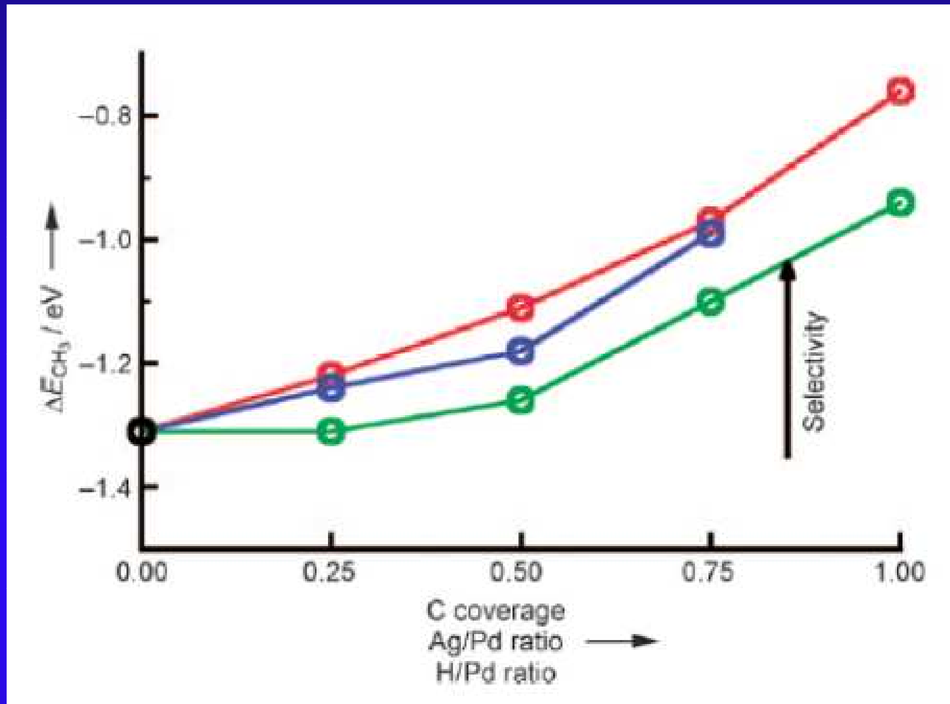
Example 3



Differential adsorption energy of a methyl group as a function of the carbon coverage as well as the Ag/Pd and H/Pd ratios. Red: palladium with subsurface carbon, blue: Pd-Ag alloys, green: palladium hydrides. Weakening of the adsorption energy of methyl groups should increase the selectivity towards ethylene.

Norskov et al.: Angew. Chem. Int. Ed. 47 (2008) 9299.

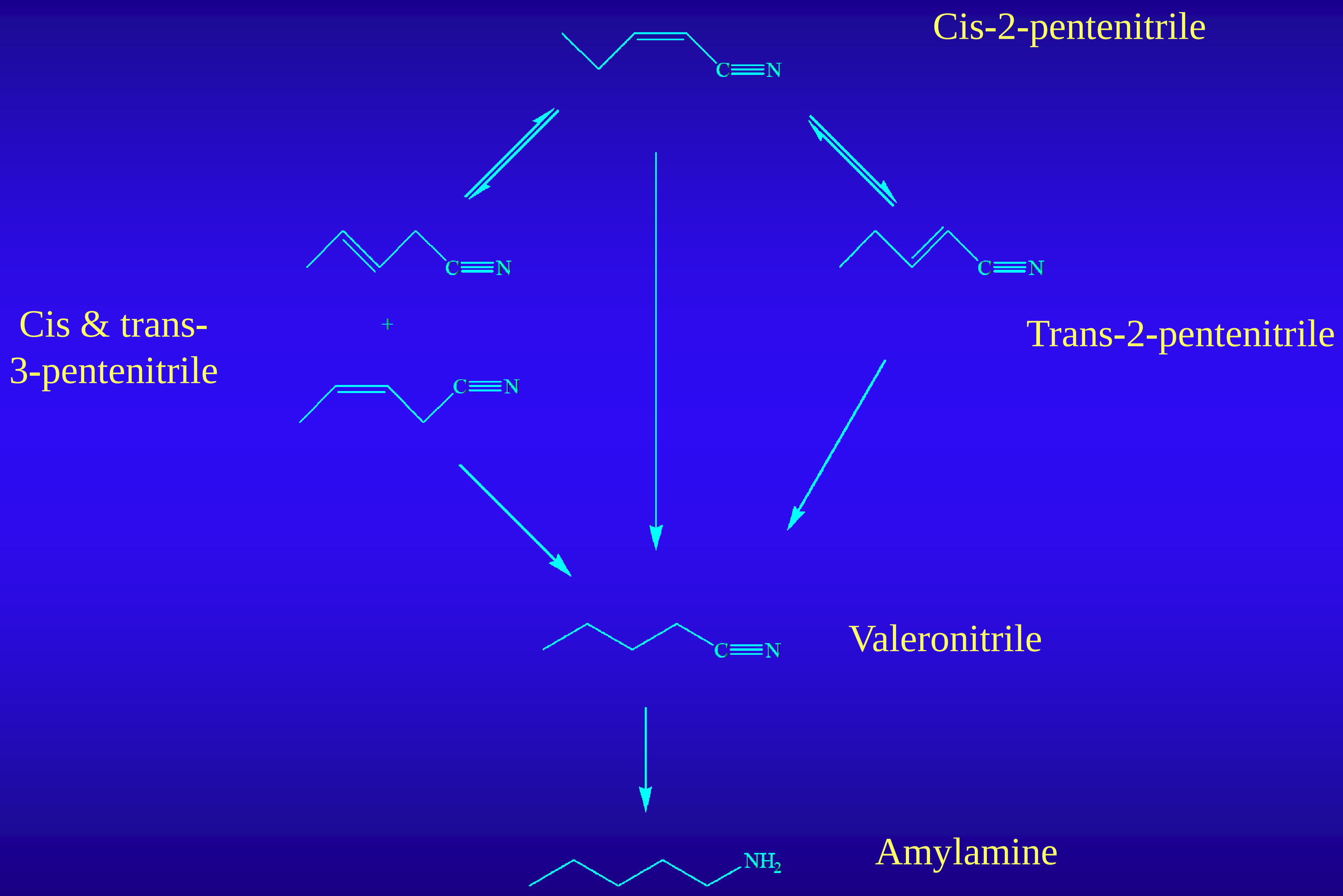
Example 3



WRONG FOR H!!

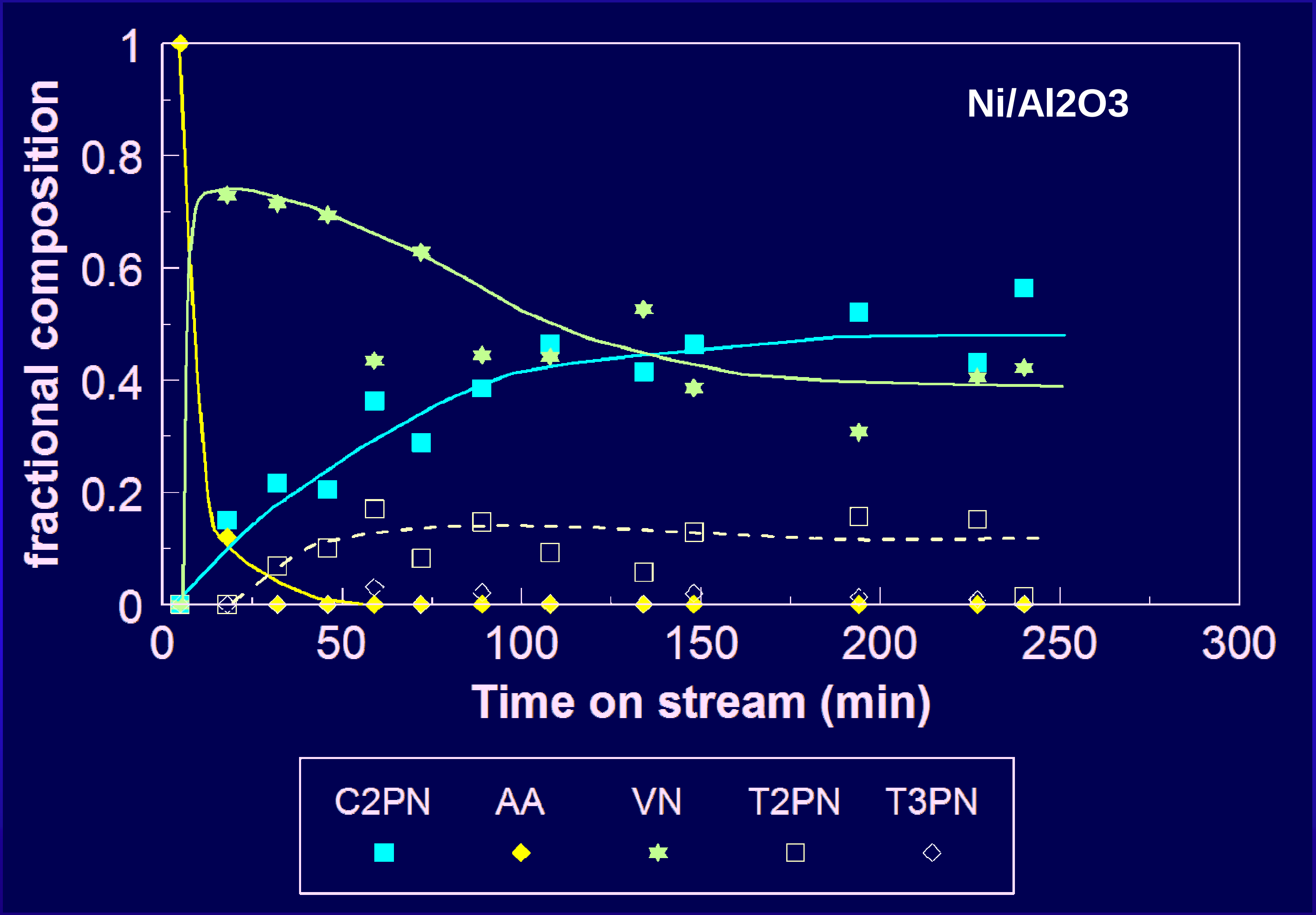
Norskov et al.: Angew. Chem. Int. Ed. 47 (2008) 9299.

Intermezzo



Cis-2-pentenitrile
C≡N
C≡N
Cis & trans-
3-pentenitrile
+
C≡N
C≡N
Trans-2-pentenitrile
C≡N
Valeronitrile
NH2
Amylamine

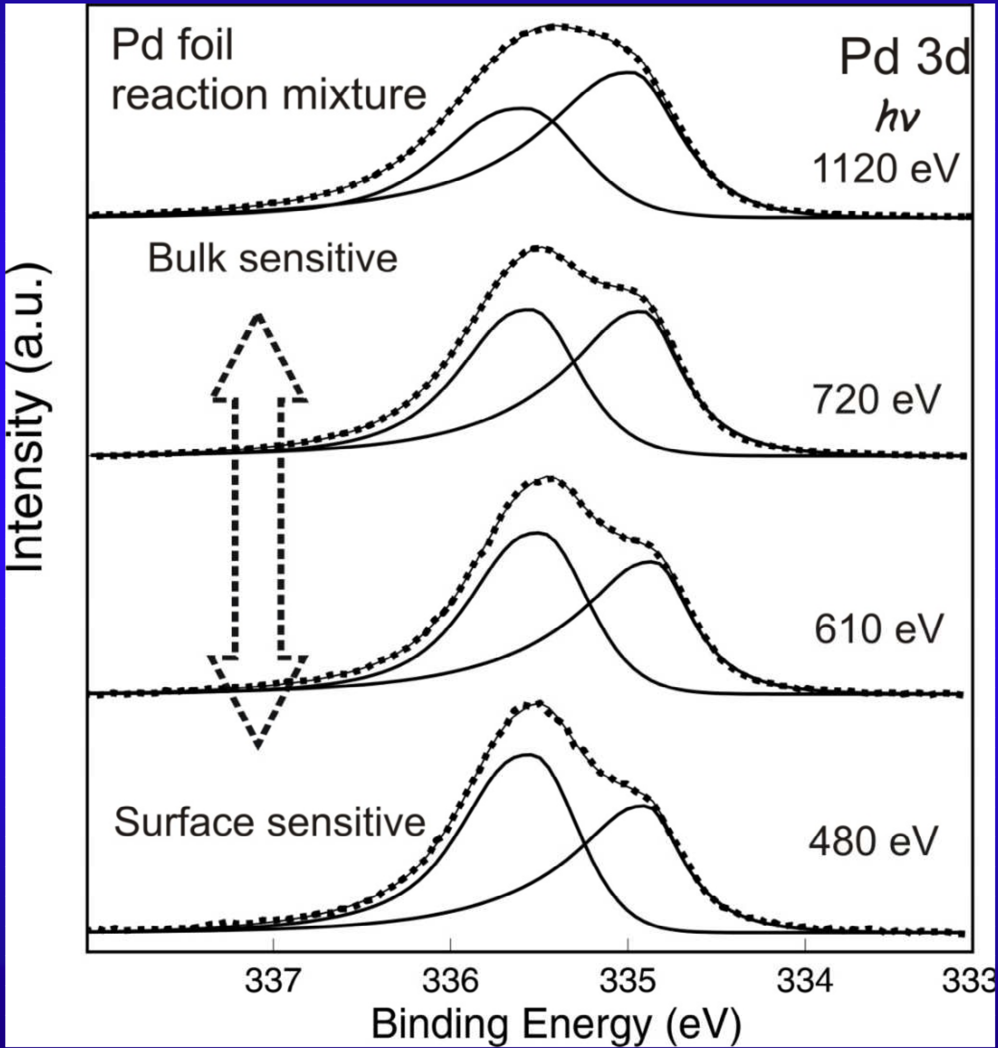
Intermezzo



Ni/Al2O3
fractional composition
0
0.2
0.4
0.6
0.8
1
0
50
100
150
200
250
300
Time on stream (min)
C2PN
AA
VN
T2PN
T3PN

Example 3: In-situ XPS: Pd 3d: sub-surface C

1-pentyne hydrogenation

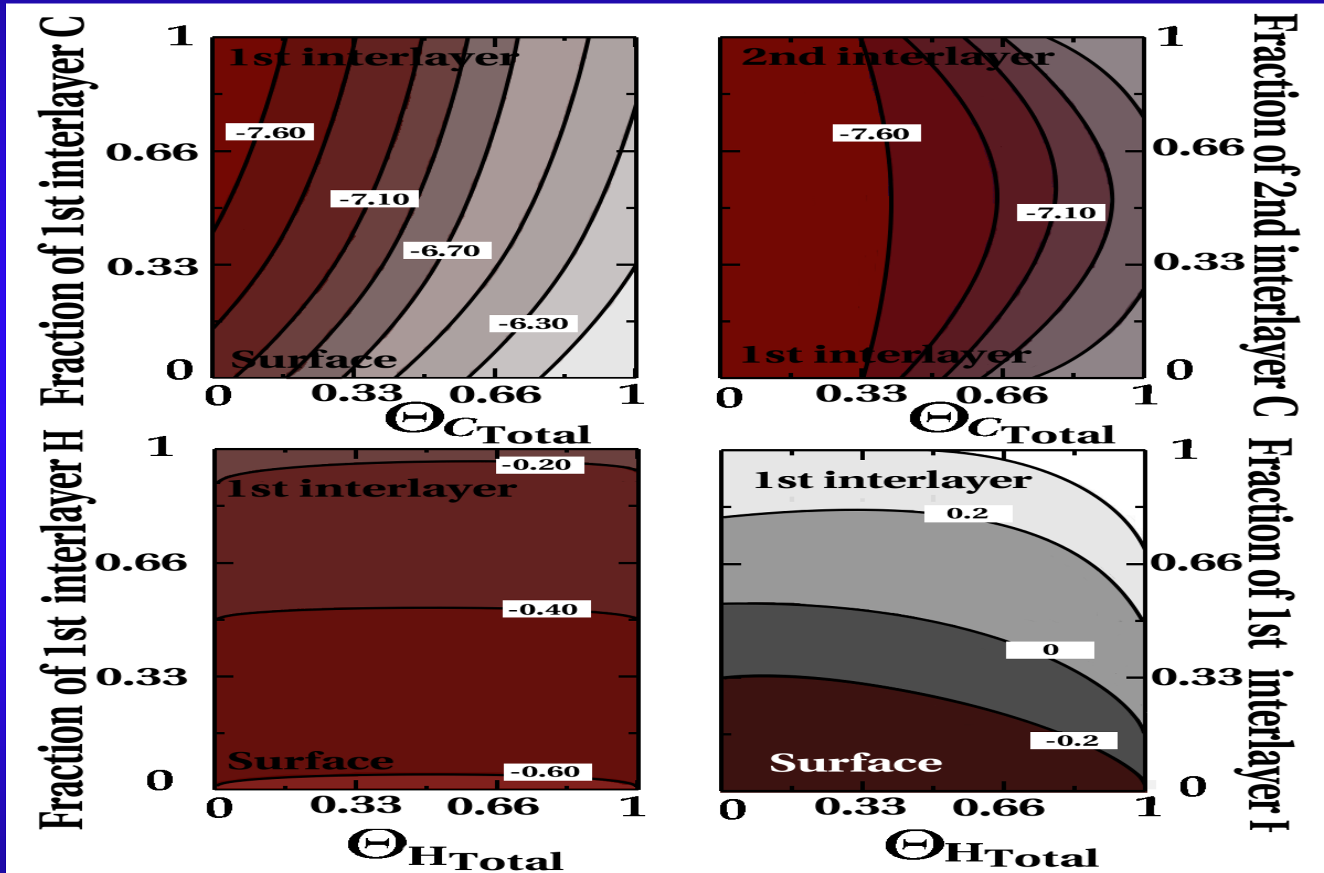


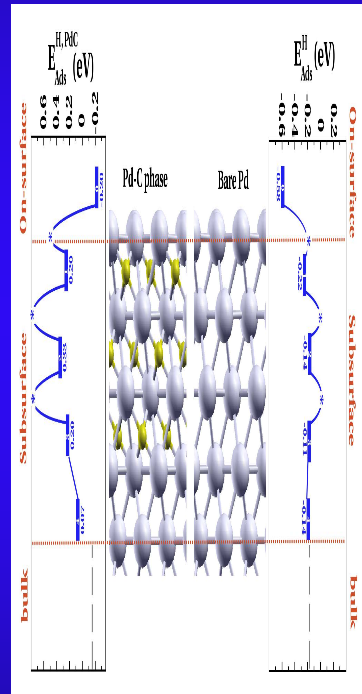
unambiguous localisation of carbon-induced component in the surface-near region BUT: not one layer

Hydride excluded

J. Catal. 242 (2006) 26.

Example 3

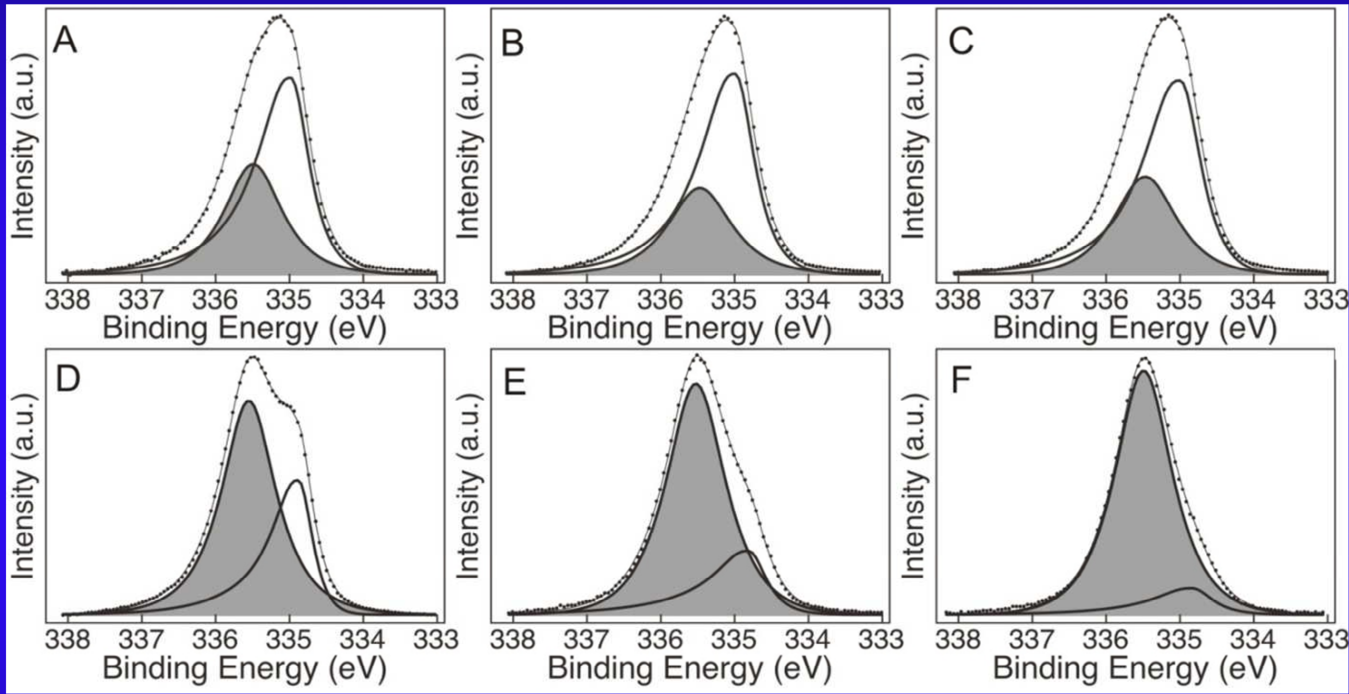




Angew. Chem. Int. Ed. 47 (2008) 9274.

Example 3

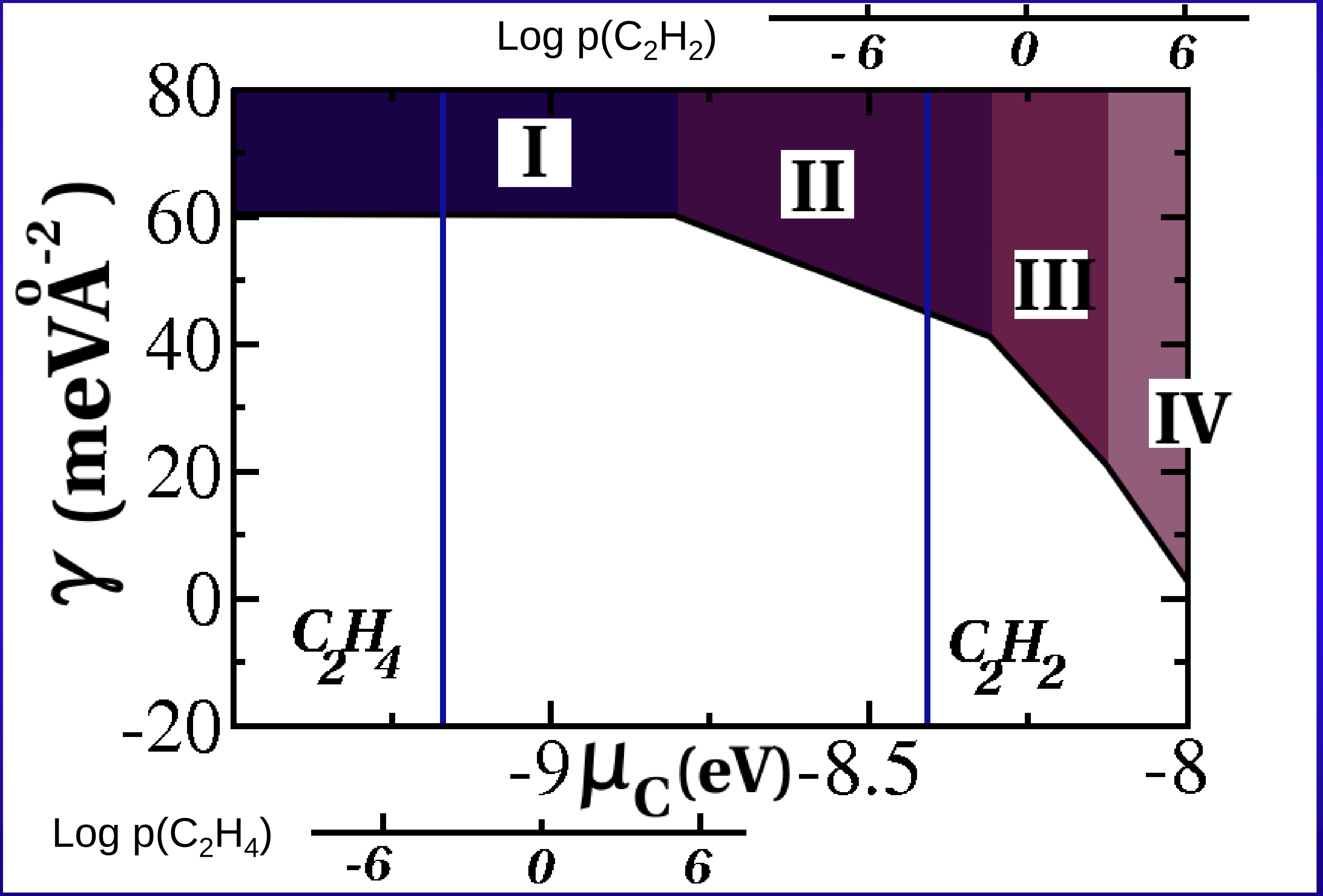
C5 C3 C2



alkynes: Pd-C
alkenes: no Pd-C

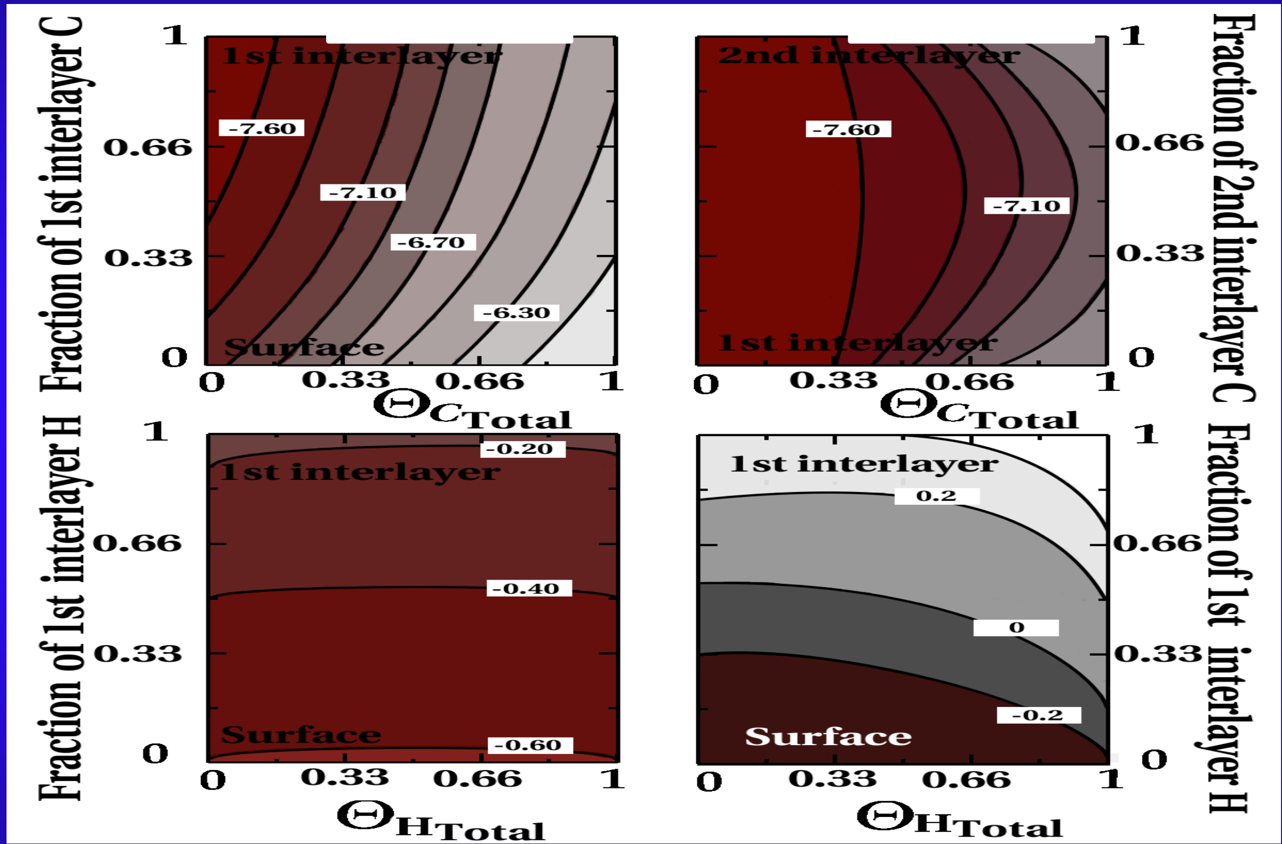
Angew. Chem. Int. Ed. 47 (2008) 9274.

Example 3



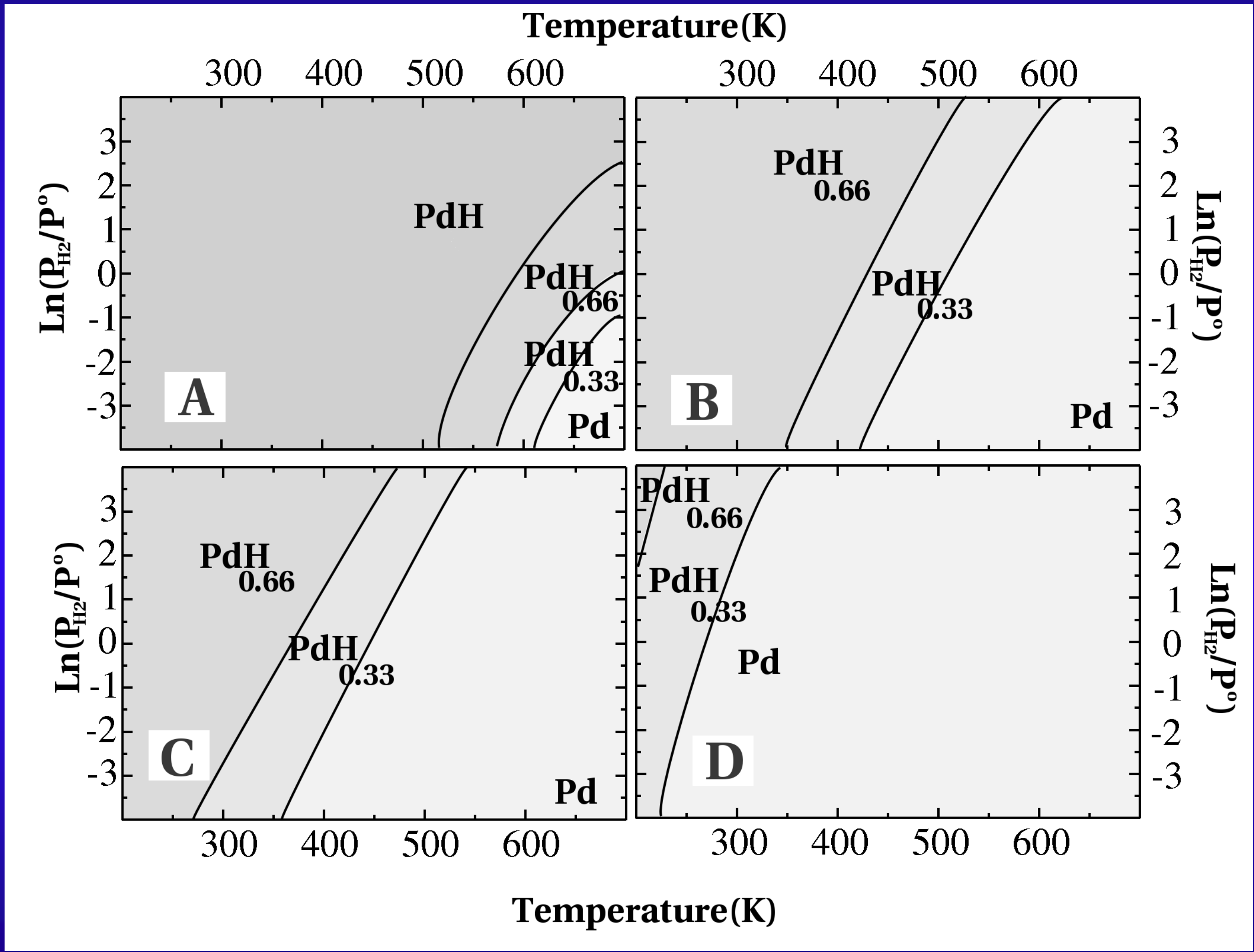
Angew. Chem. Int. Ed. 47 (2008) 9274.

Example 3



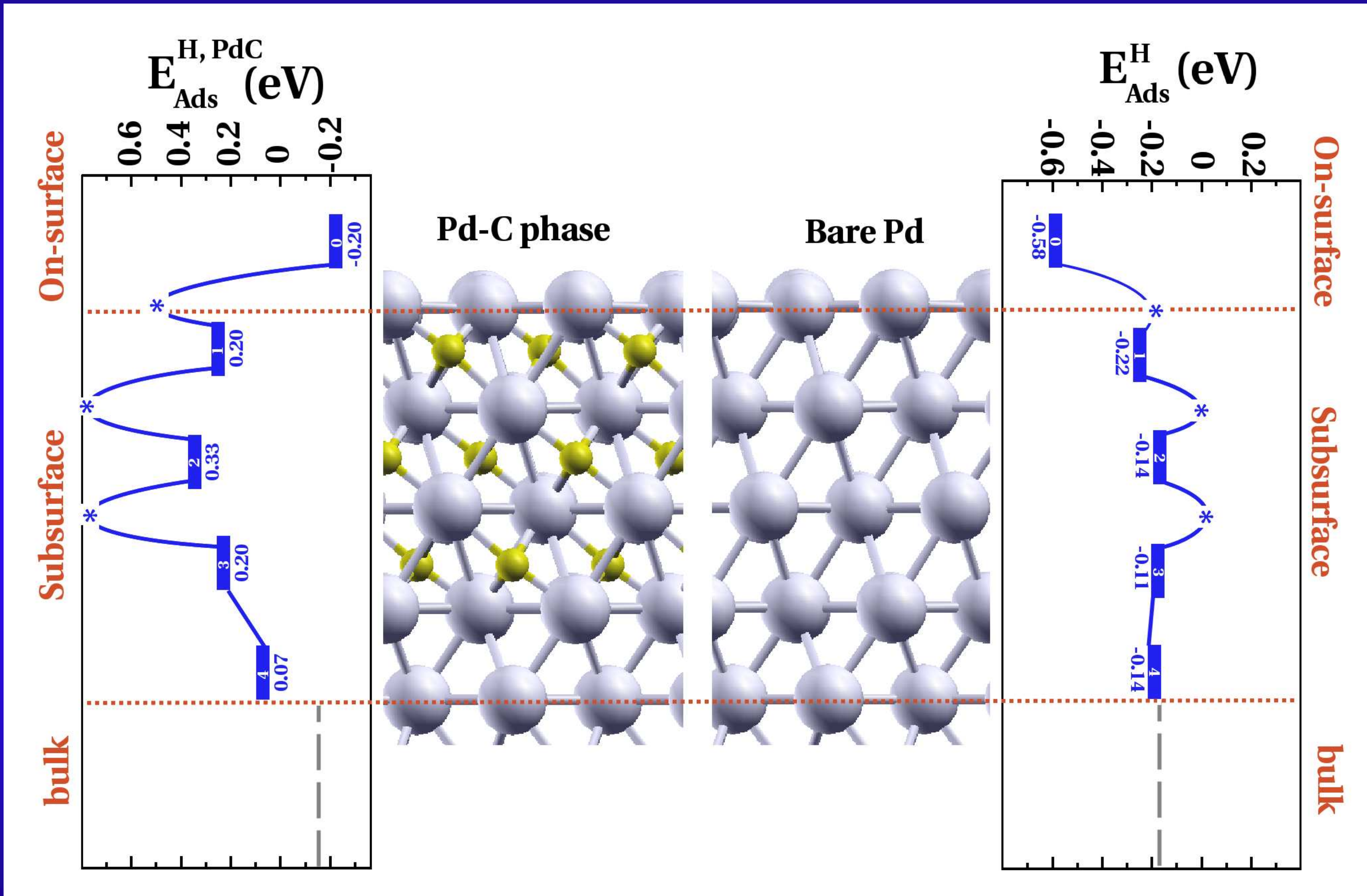
Angew. Chem. Int. Ed. 47 (2008) 9274.

Example 3



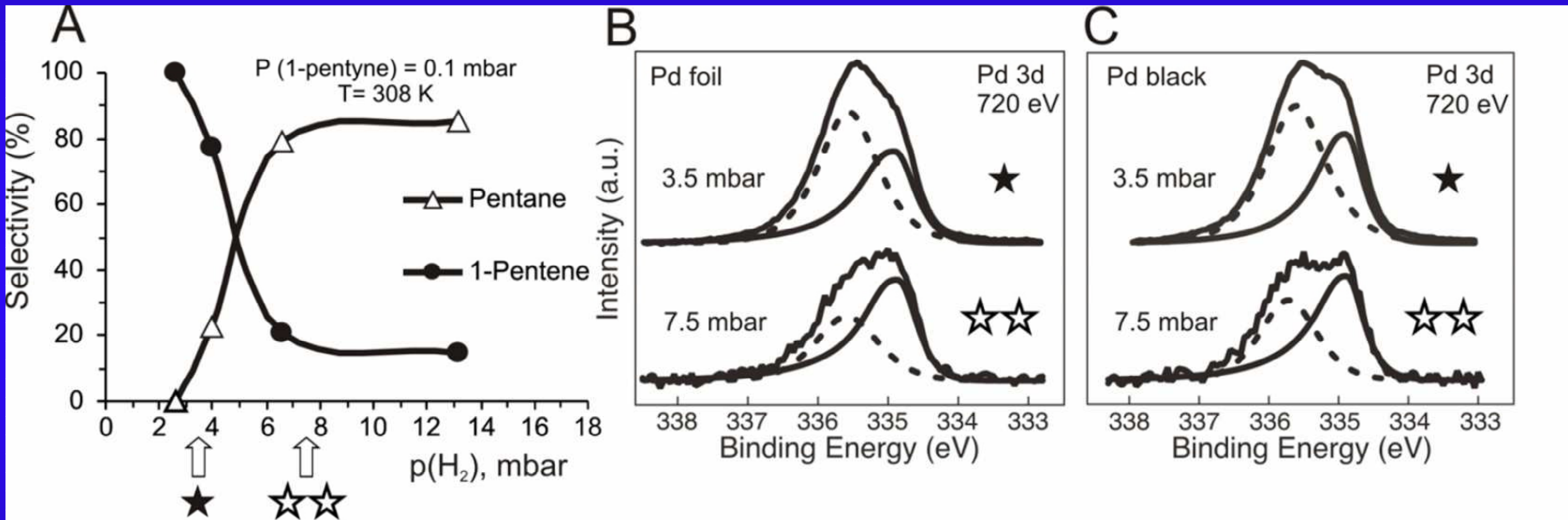
J. Phys.Chem.C. in press.

Example 3: H diffusion barriers



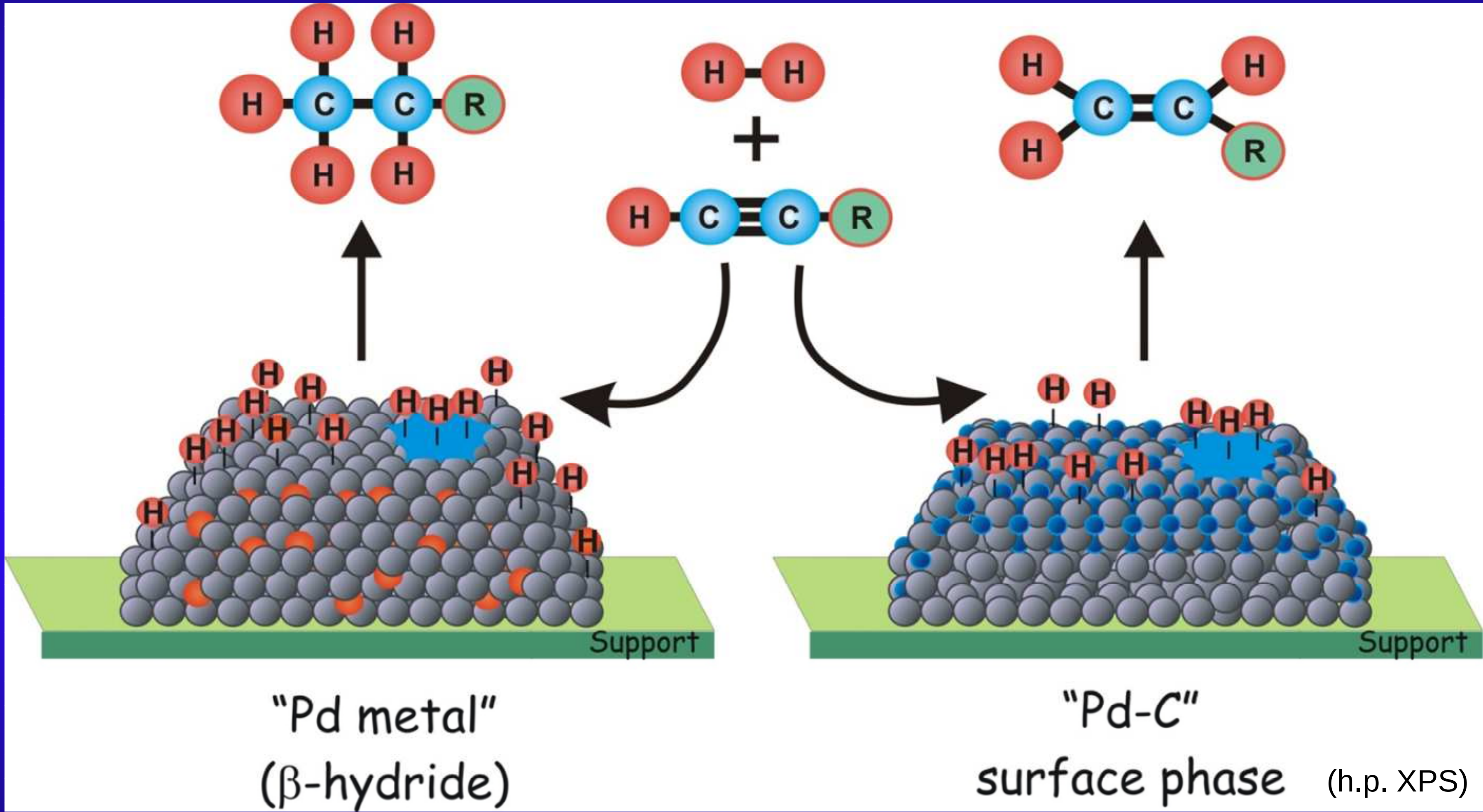
J. Phys.Chem.C. in press.

Example 3



Selective hydrogenation with Pd-C
Non-selective hydrogenation with Pd

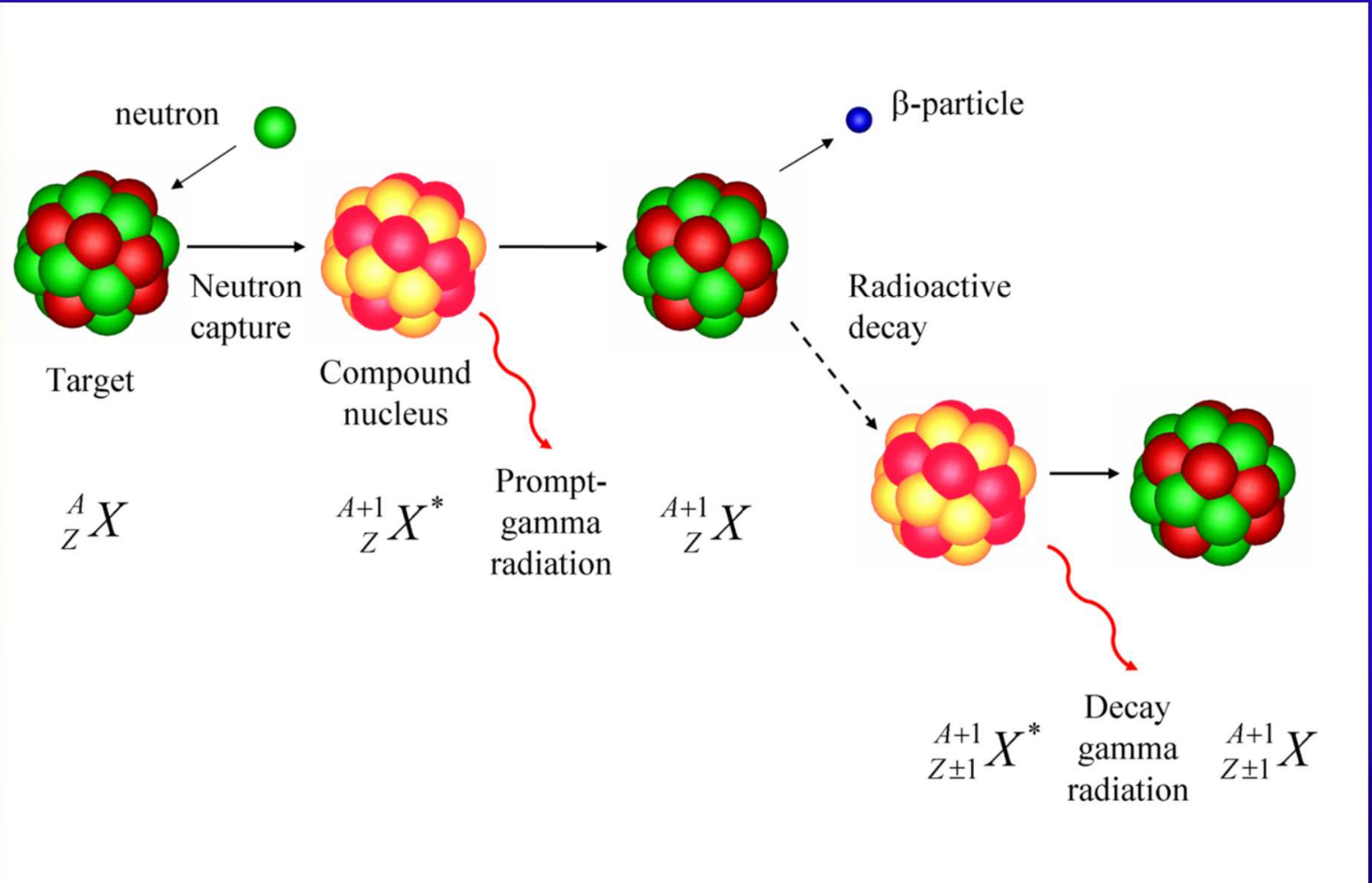
Example 3



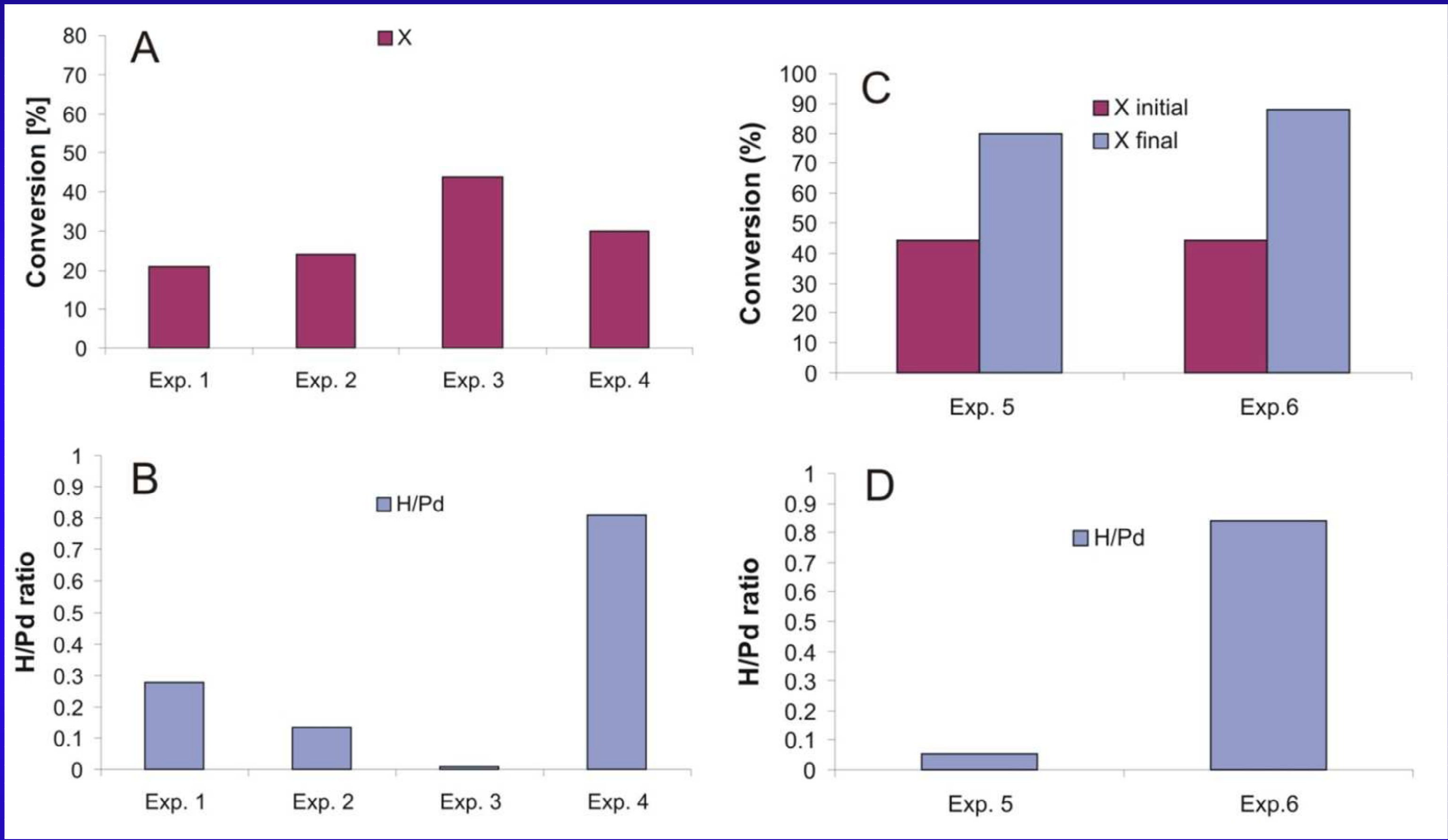
Science 320 (2008) 86.

In situ PGAA

Hydrogenation → **Quantitative determination of H uptake**



Example 3: In situ PGAA



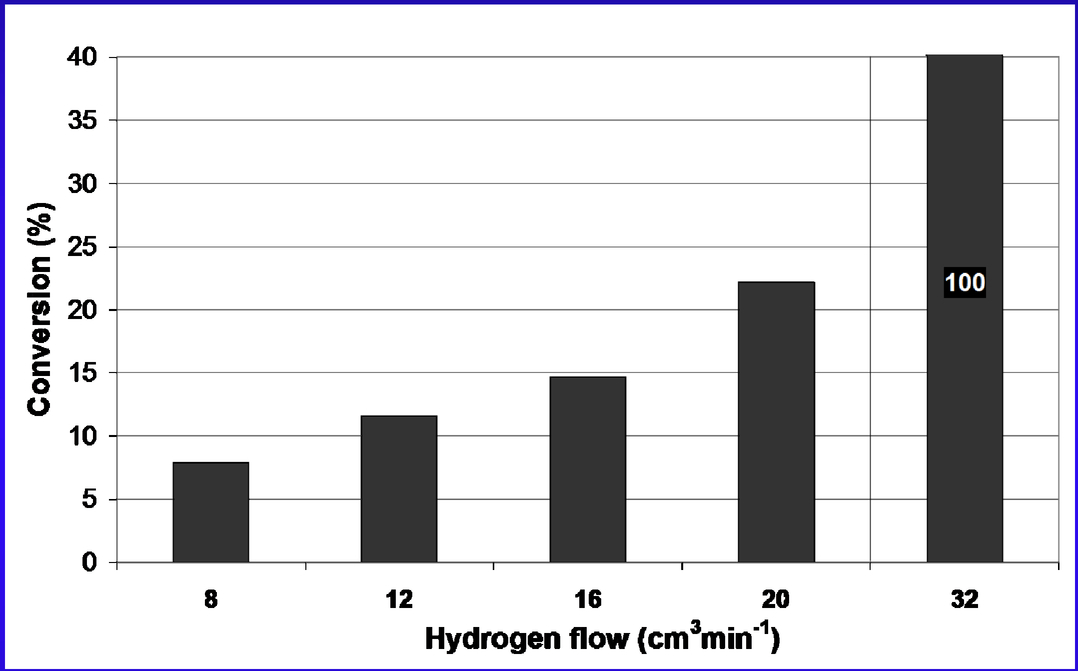
No correlation between activity and H/Pd in selective C_5H_8 hydrogenation, despite the first order $p(H_2)$ rate dependence. Bulk is decoupled.

Exp. 1-4: identical conditions

Exp. 5-6: identical conditions

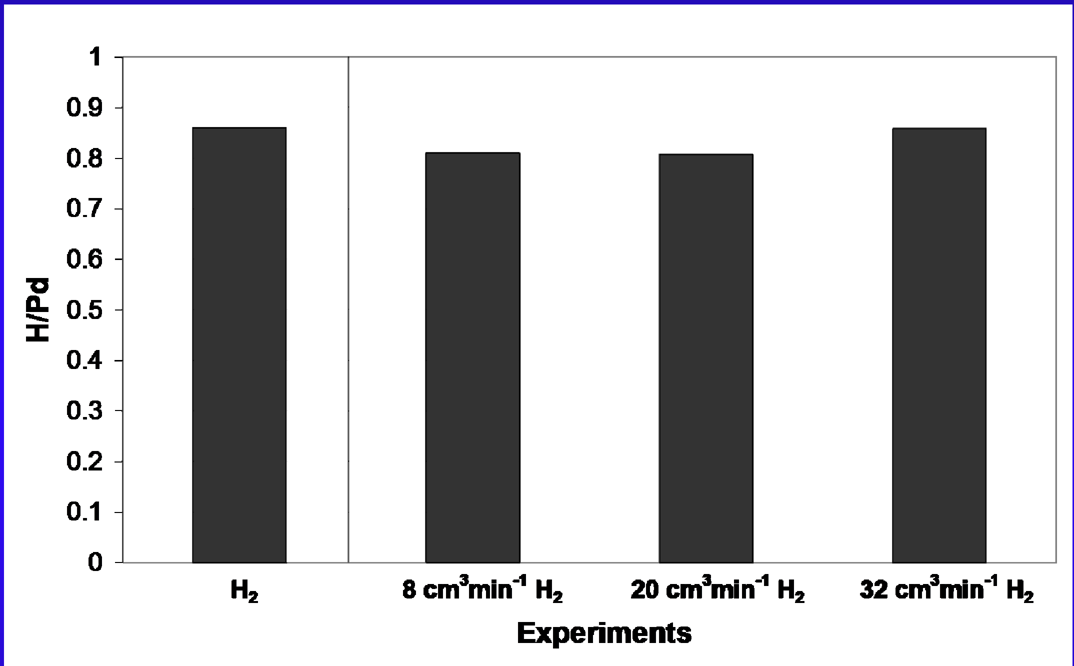
Example 3

Selective Non-s.



Propyne hydrogenation: first order for $p(H_2)$

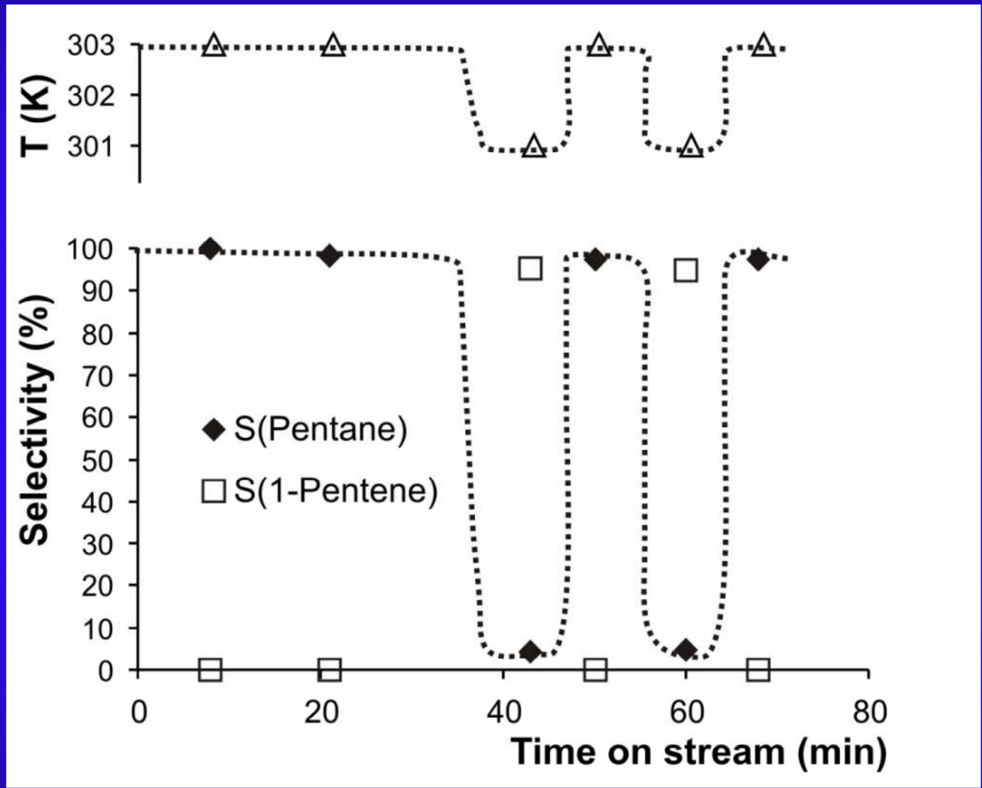
Example 3



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
H/Pd
H_2
8 $cm^3 min^{-1}$ H_2
20 $cm^3 min^{-1}$ H_2
32 $cm^3 min^{-1}$ H_2
Experiments

Example 3

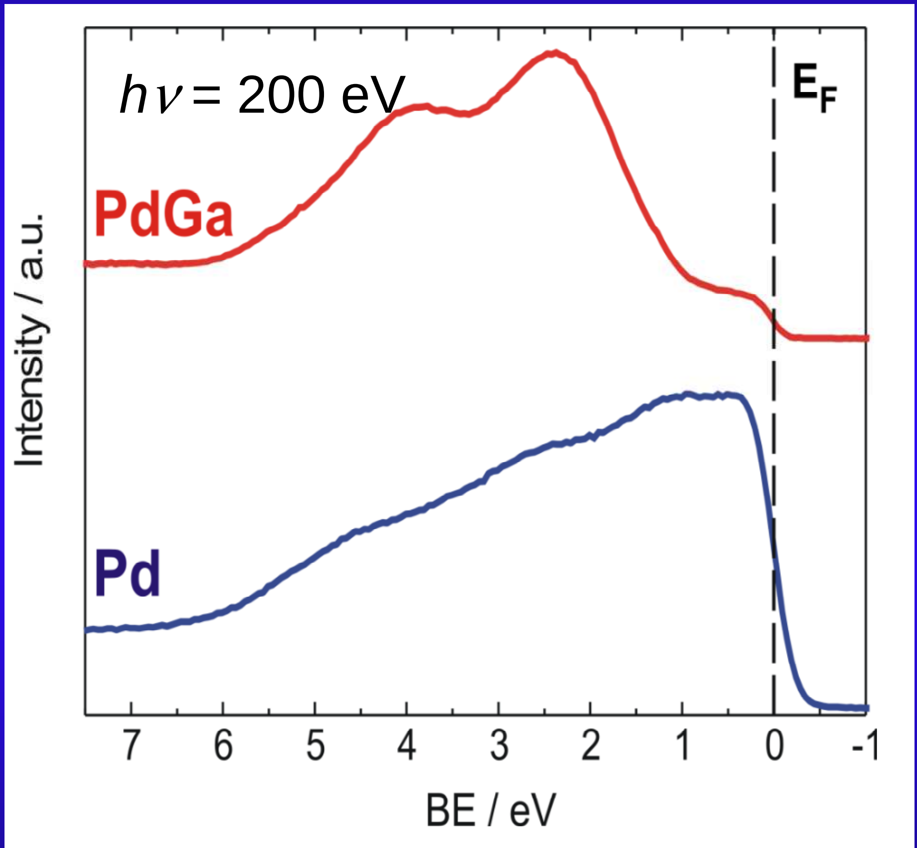
Kinetic discontinuity; oscillations

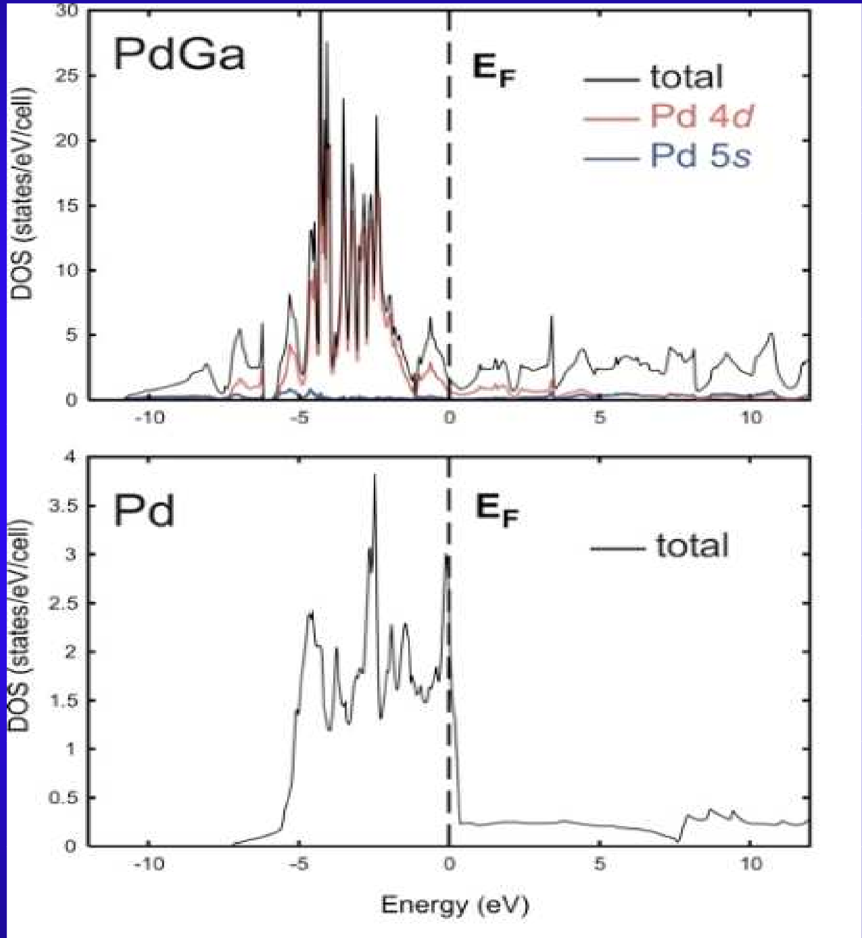


Adiabatic reactor

Control of selectivity: issue!

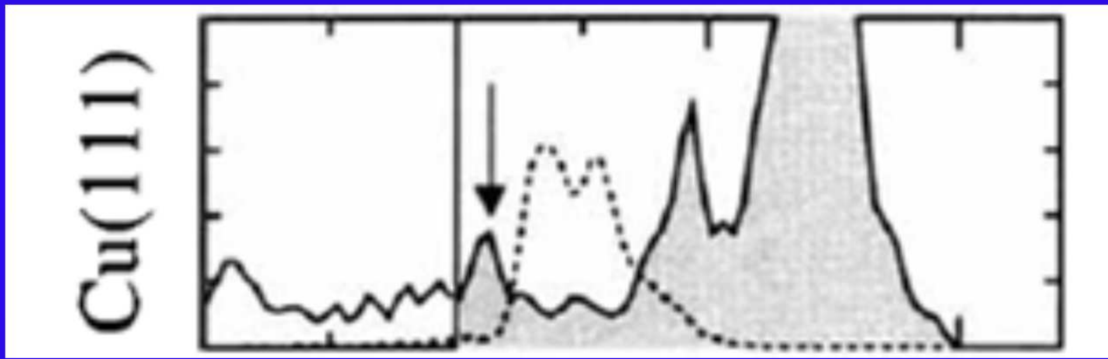
Example: PdGa





Question

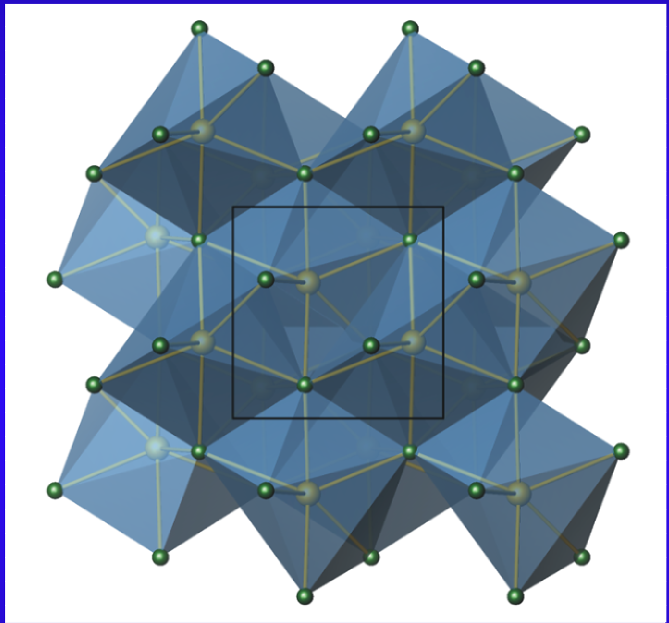
DOS, VB of PdGa looks like…?



From slide 9…

Example: PdGa

PdGa



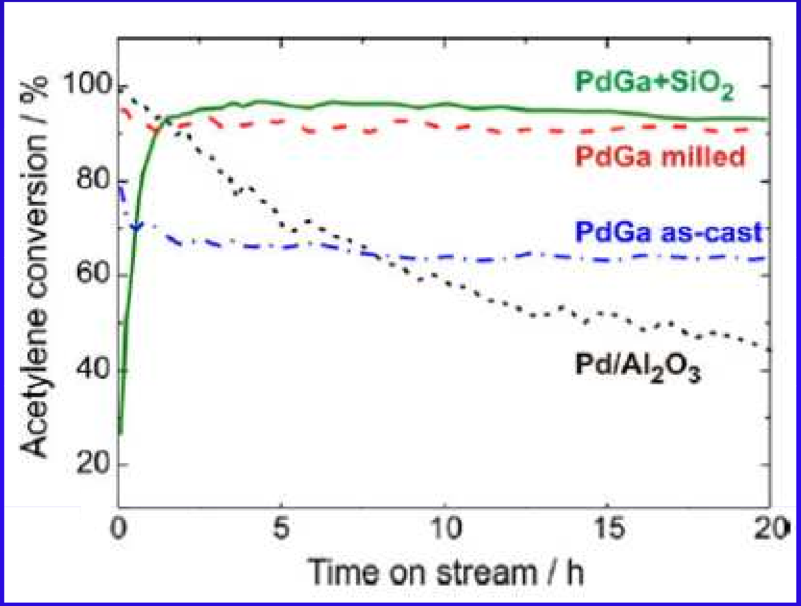
Isolated Pd site

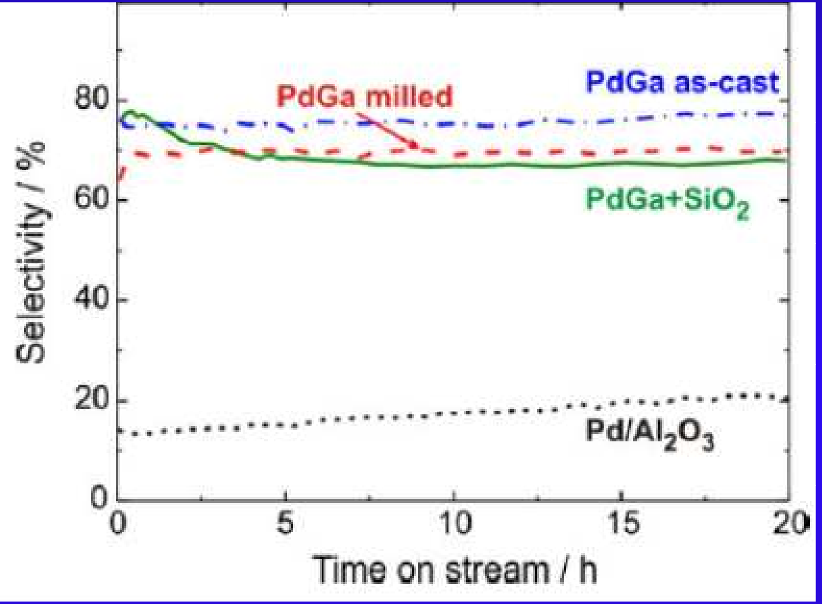
- Covalent bonding
- Modified electronic structure

No H dissolution (PGAA)

Excellent selectivity in acetylene semi-hydrogenation

Example: PdGa





Kovnir et al.: Surf. Sci. 603 (2009) 1784.

Example: competitive reaction

over Pd/C

Initial rates for alkyne hydrogenation

Second component	Initial rates[a] of hydrogenation[b]			
	Phenyl acetylene	1-Phenyl-1-propyne	1-Pentyne	2-Pentyne
Phenyl acetylene	84.2	–	5.8	4.1
1-Phenyl-1-propyne	–	32.9	12.8	12.5
1-Pentyne	5.4	0.5	18.7	59.7
2-Pentyne	15.2	4.4	101.0	40.1

[a] Rates in $mmol\, g^{-1}\, min^{-1}$.

[b] The table is symmetric about the diagonal axis for competitive reactions. The results on the axis are those for the compound in the absence of a second component. All other rates should be read "down". For example the rate of 1-pentyne hydrogenation in the presence of 1-phenyl-1-propyne is 12.8, while the rate of 1-phenyl-1-propyne hydrogenation in the presence of 1-pentyne is 0.5.

Jackson et al.: Appl. Cat. A 237 (2002) 202.

Competitive reactions are sometimes difficult to predict!

Example 4: Edible Oils

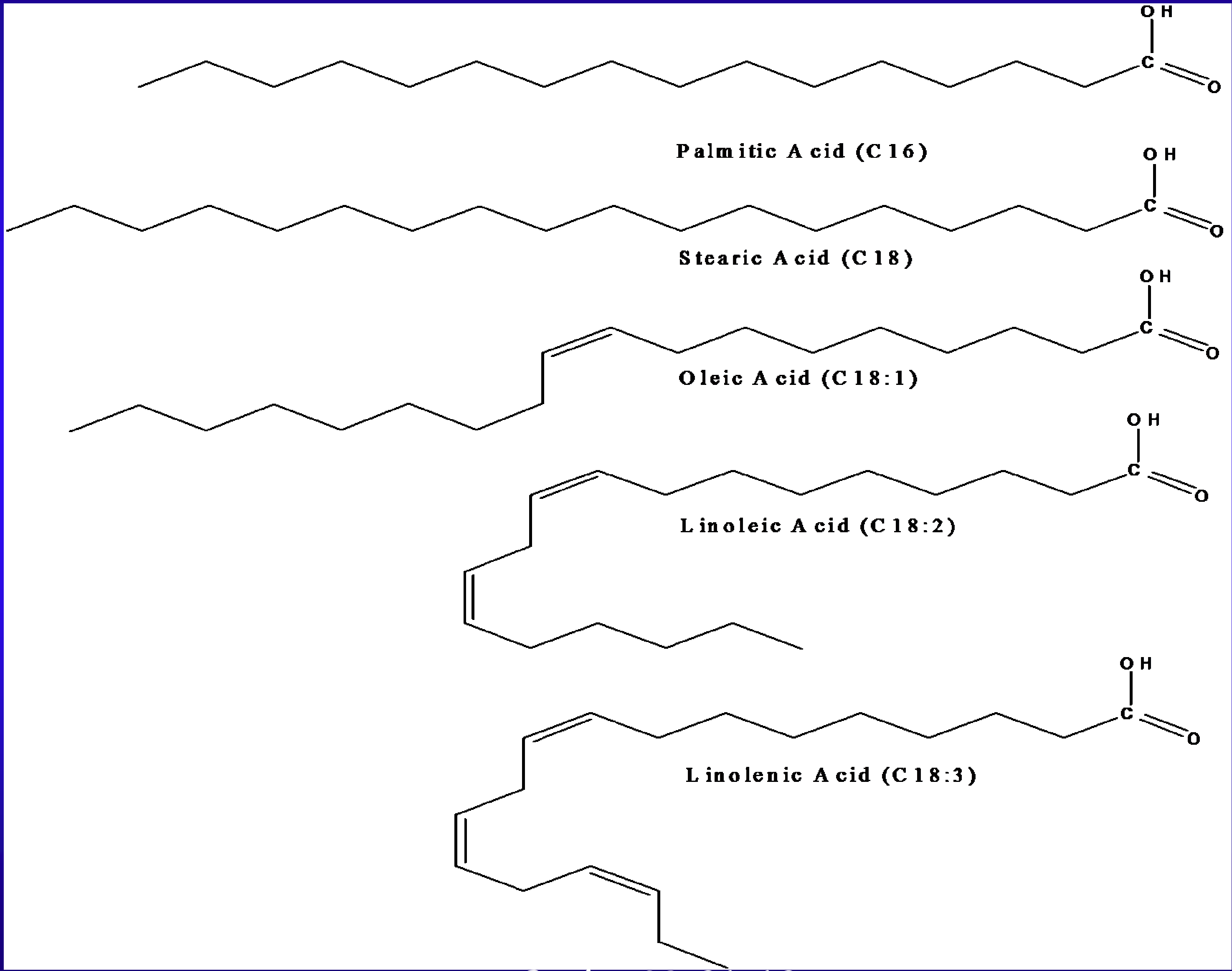
Edible oils (sunflower,soybean) consist of long chain fatty acids- C16 to C18

Mixtures of saturated (SFA), mono (MFA) - and polyunsaturated (PFA) fatty acids

MFA and PFA can exist in *cis* or *trans* configuration

Research shows *trans* fatty acids (TFA) lead to high LDL cholesterol: BAD!

Example 4


OH
C
O
Palmitic Acid (C16)
Stearic Acid (C18)
Oleic Acid (C18:1)
Linoleic Acid (C18:2)
Linolenic Acid (C18:3)

Example 4

Hydrogenation of edible oils necessary to produce solid foods such as margarine PFA, MFA

Isomerization of cis fatty acids to trans fatty acids can occur during hydrogenation

Development of hydrogenation catalysts which offer higher selectivity to products with cis configuration and lower selectivity towards SFA formation is of great commercial interest

Nickel Systems

High TFA content 15-30%

H_2 surface concn – Low = TFA
High = SFA

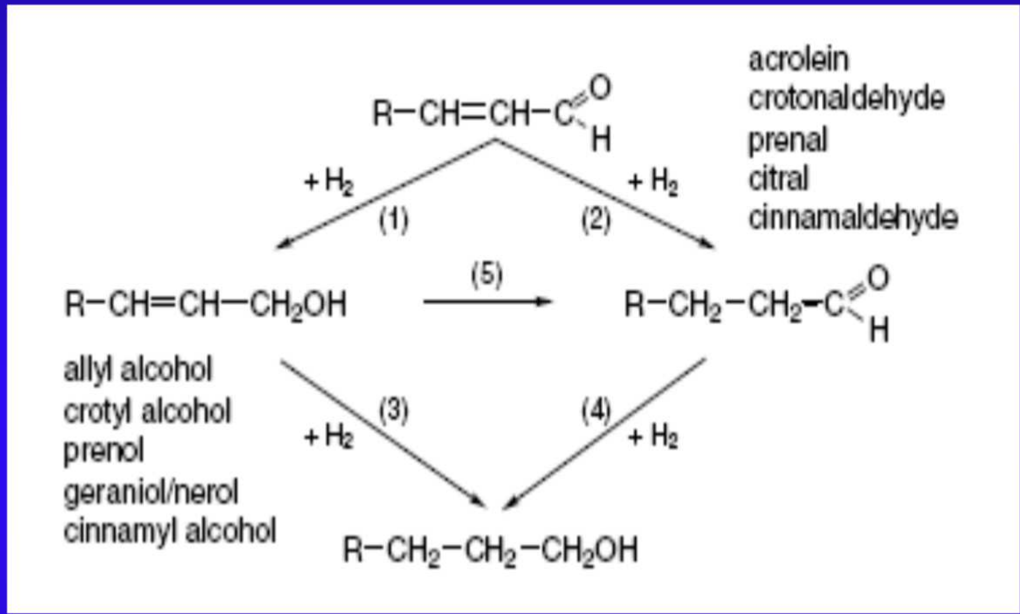
Low Temperature – Low TFA

Platinum Systems

More active

Lower TFA content (8%)

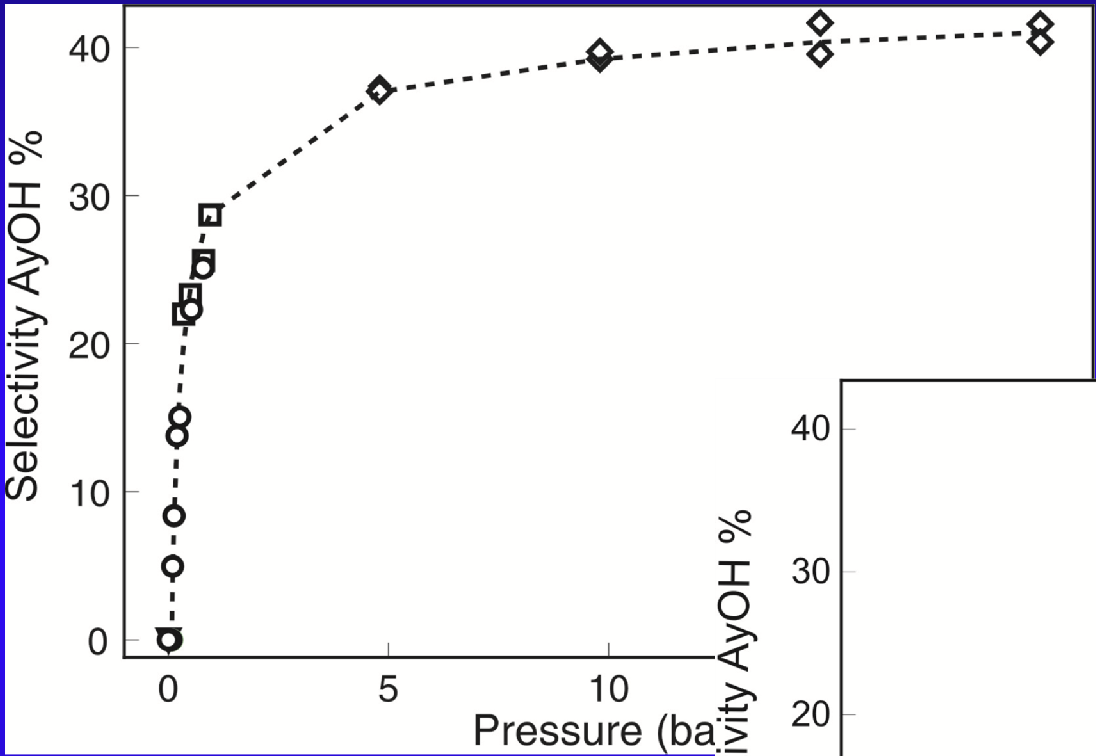
Example 5: Regioselectivity

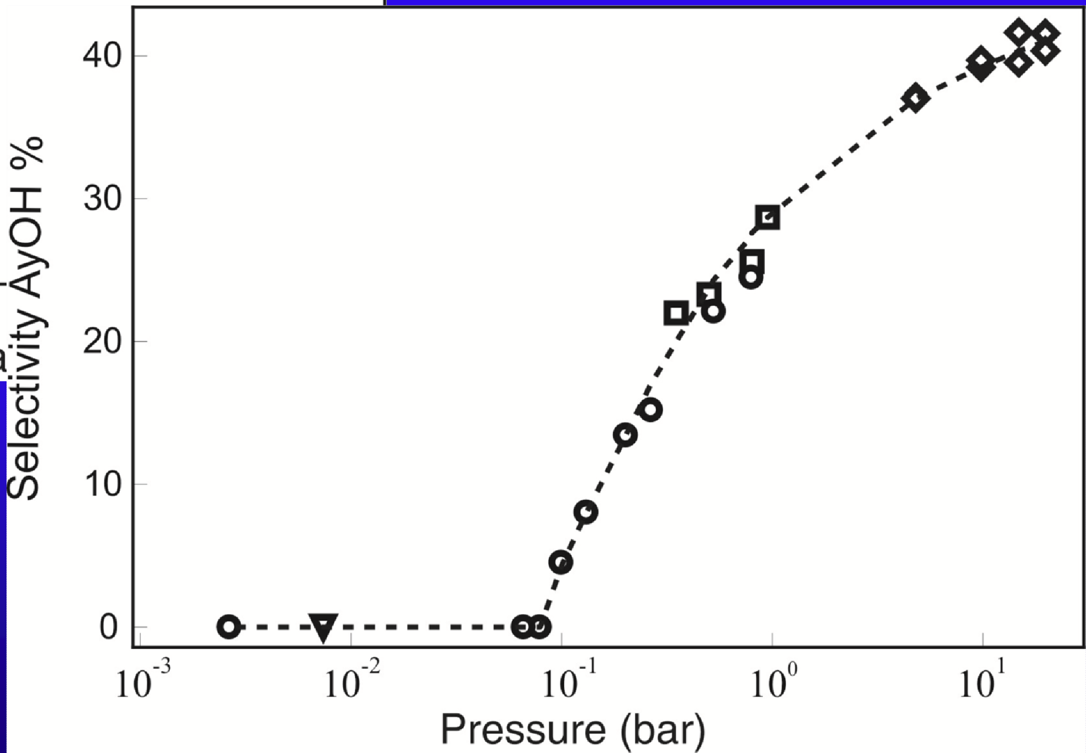


Effect of “R”: sterical hindrance

Example 5

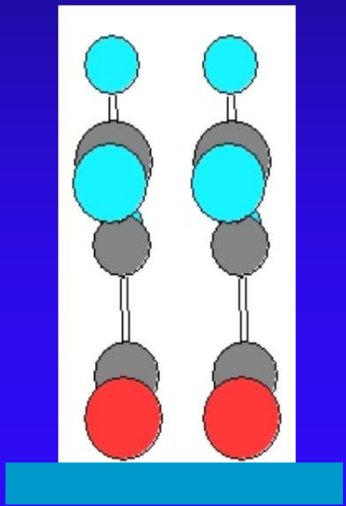
Ag/SiO_2





Bron et al.: PCCP 9 (2007) 3559.

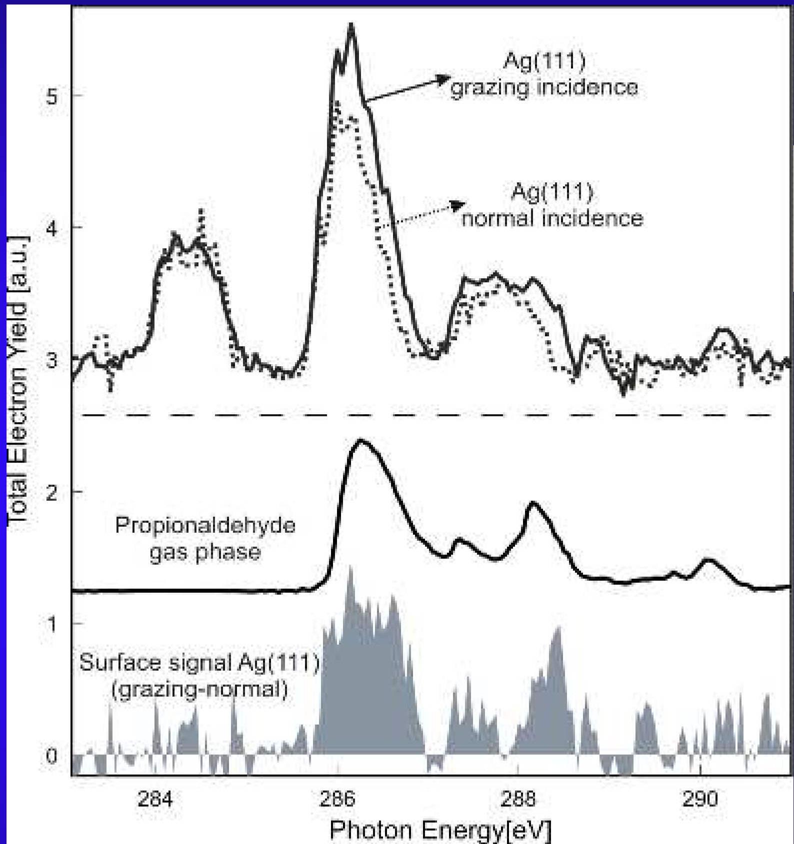
Selectivity control

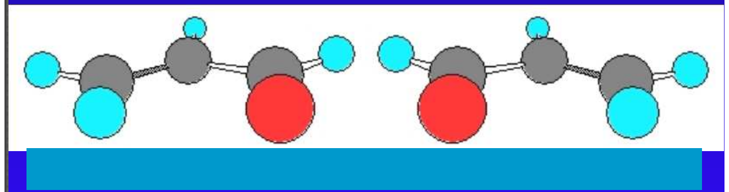


standing

AyOH

high pressure
rough





flat-lying

POH

low pressure
flat

Size of Ag terrace, Roughness of Ag, Pressure of acrolein

Example 6: C_6H_6 hydrogenation

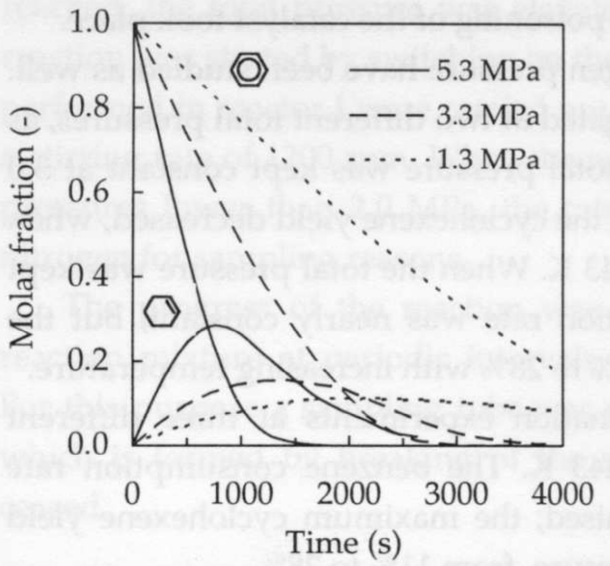


Figure 5: Influence of the hydrogen pressure on the course of the partial benzene hydrogenation. For clarity the profiles of cyclohexane are left out. Experimental conditions: 0.5 g Ru-B, 200 ml benzene, 150 ml water, 2.4 g iron sulfate, temperature 443 K, reactor I.

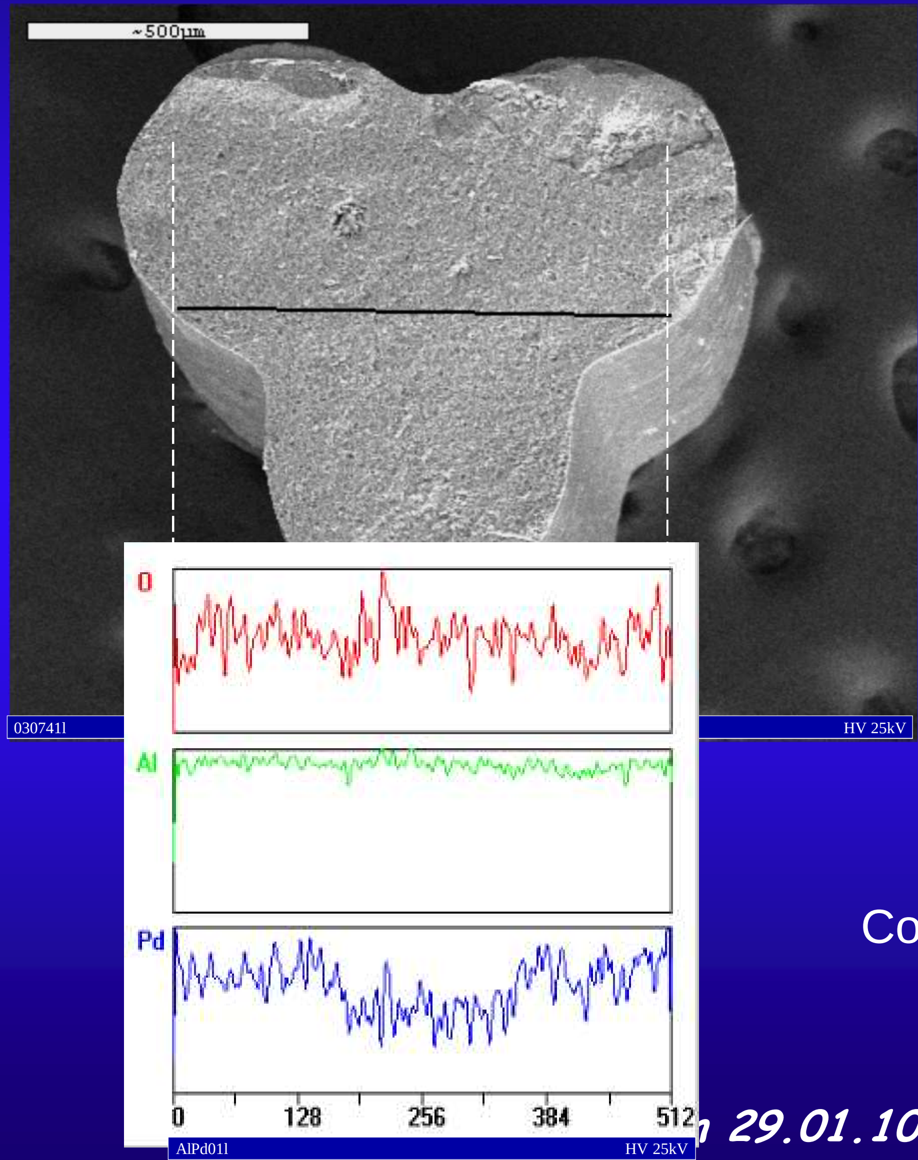
Increasing H_2 partial pressure <u>increases</u> the selectivity of the partial hydrogenation product (cyclohexene)!

complex interplay of mass transfer limitations?

Soede: PhD thesis

Engineering

Engineering

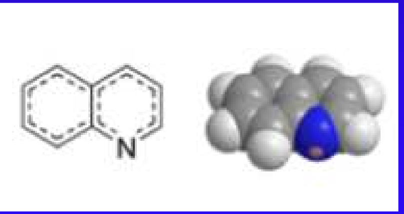


Core-shell structure to avoid
secondary reaction

Engineering

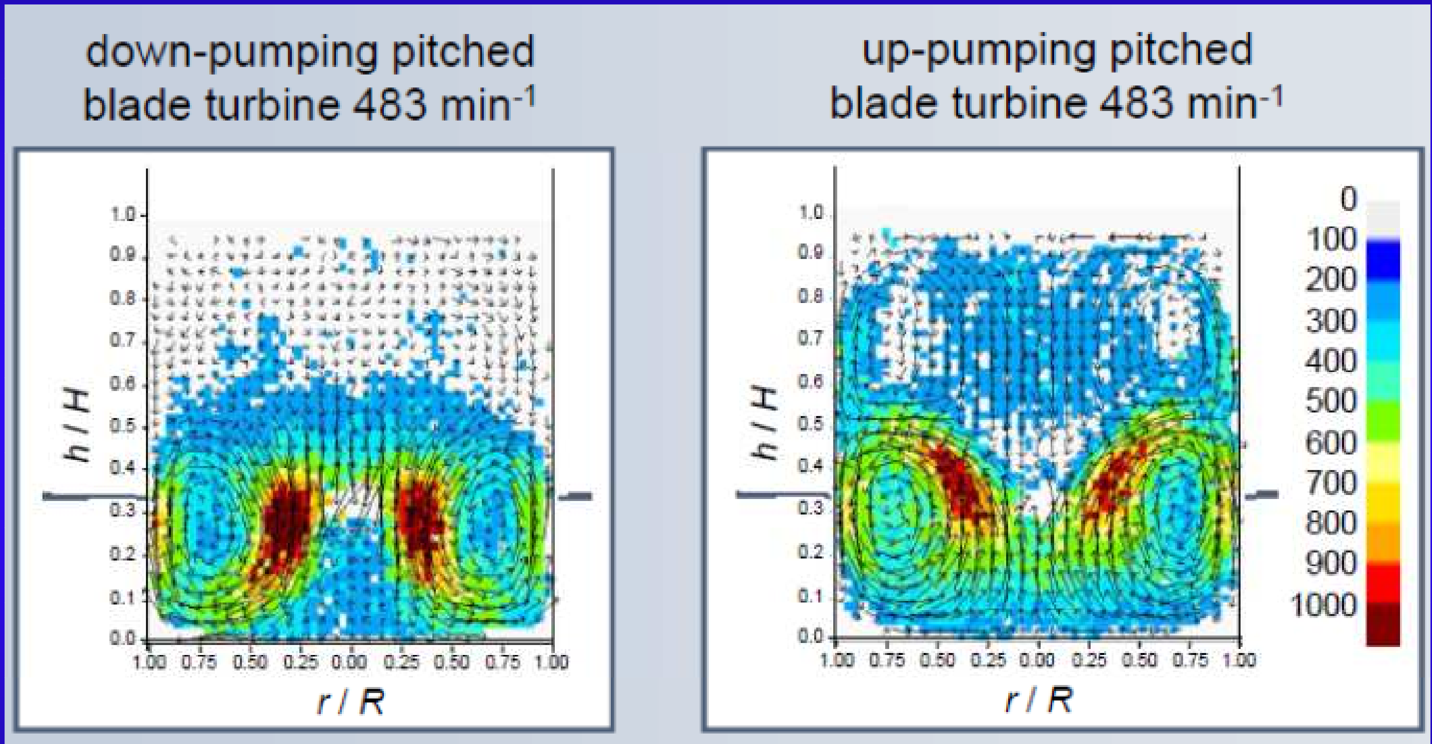
Lindlar catalyst: Pd on $CaCO_3$ (non-porous!) deactivated with Pb and quinoline

Vitamin A synthesis



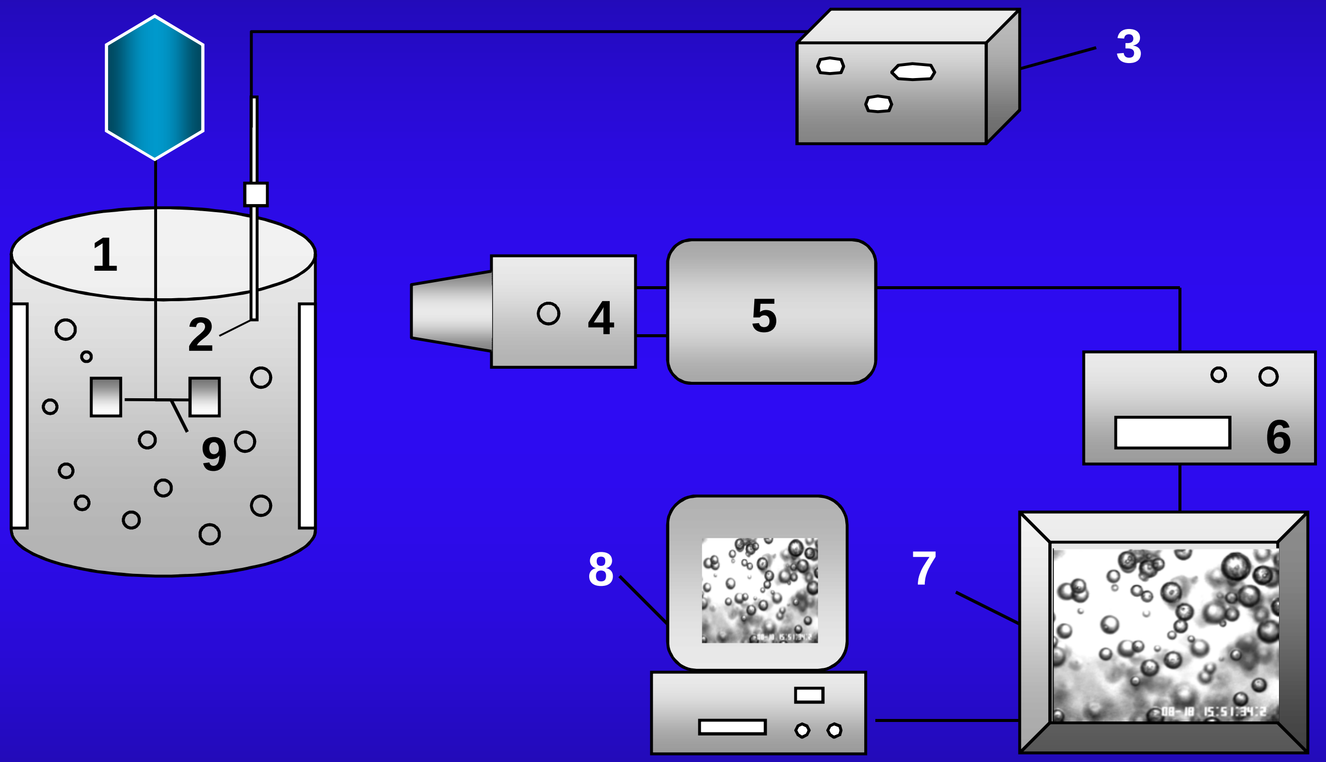
Schlögl et al.: HELVETICA CHIMICA ACTA 70 (1987) 627.

Engineering



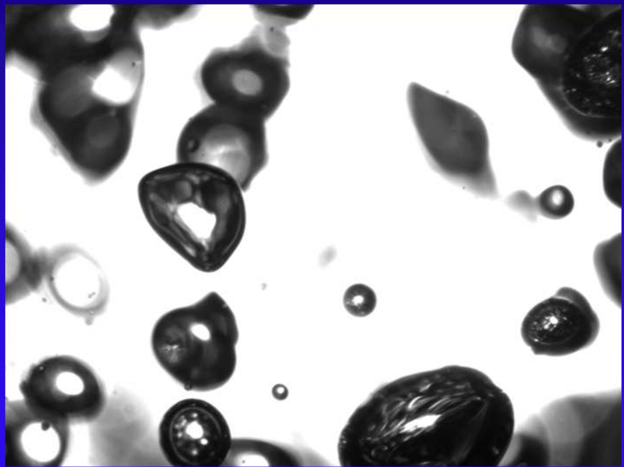
Gas-hold up is considerably higher for up-pumping than down-pumping PBT.

Engineering

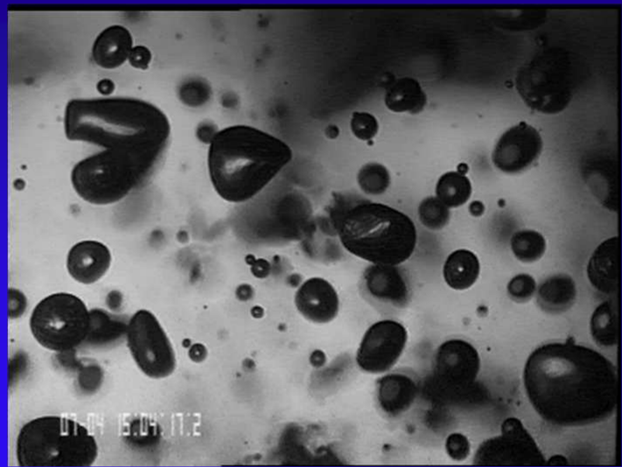


1. Stirred vessel
2. Strobe lamp
3. Strobe flash
4. Stereo microscope
5. Video camera
6. Video recorder
7. TV monitor
8. Computer
9. Impeller

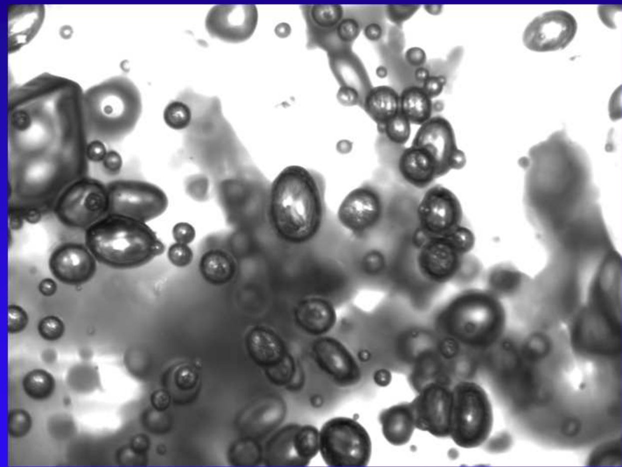
Engineering: bubble size



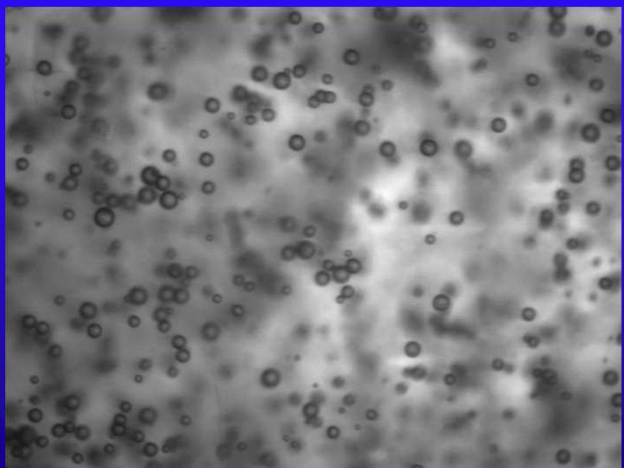
100% Water 400 μm



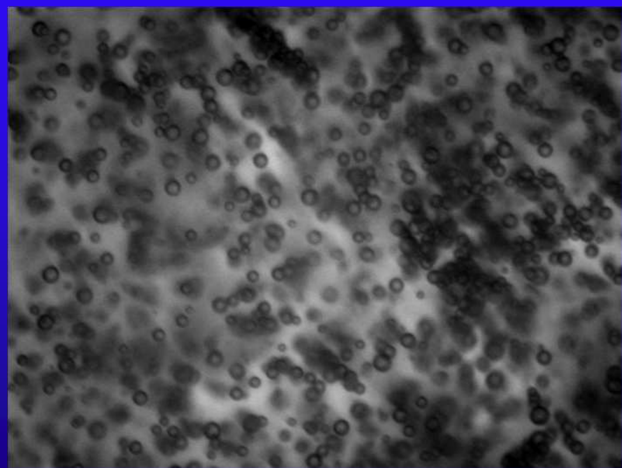
100% IPA 400 μm



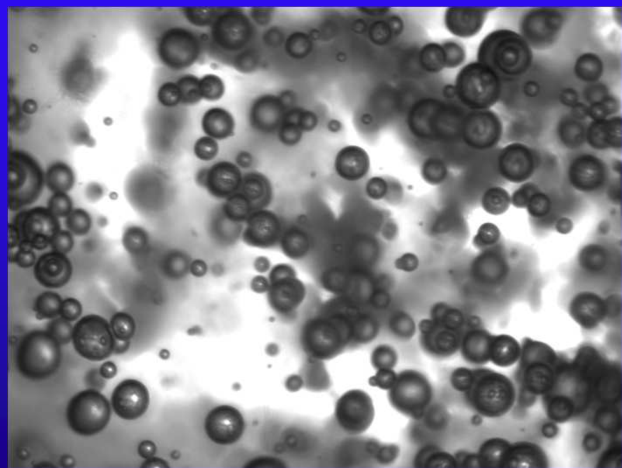
65% IPA 200 μm



1% IPA 200 μm



5% IPA 200 μm



30% IPA 200 μm

Conclusion