

Part B: Unraveling the mechanism of catalytic reactions through kinetics and thermodynamics

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Outline:

1. Why studying ethanol condensation to butanol?
2. Suggested reaction mechanisms in the literature
3. Methods:
 - Thermodynamic calculations
 - Reactor + analytics
4. Ethanol condensation over a **transition metal-free** hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
5. Other examples:
 - n-alkane hydroisomerisation
 - Methanol steam reforming
 - NO oxidation to NO_2 during SCR



“Oxo” process:
propene, CO, H₂
(Co, Rh, Ni)



Solvent, chemicals

Butanol

Aldol condensation:
Base + Metal
M-free basic solids!

Ethanol



**ABE
Fermentation**

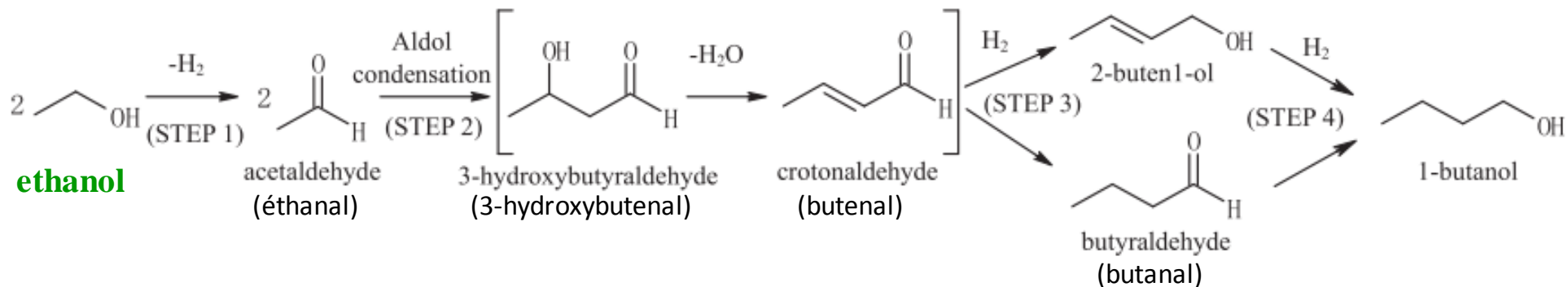


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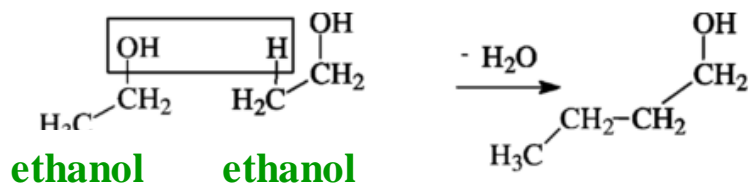
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Metal-free ethanol condensation to butanol: mechanism?

➤ « Guerbet » mechanism (Acetaldehyde self-aldolisation)



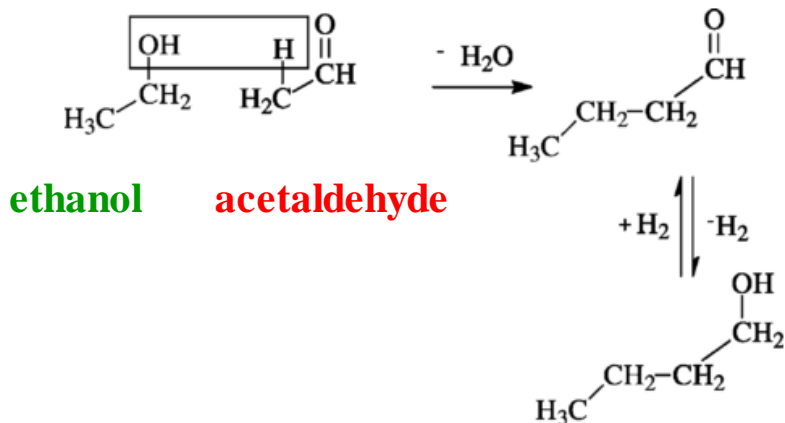
➤ Direct dimerisation



Ogo et al., *Appl. Catal. A* 402 (2011) 188

Yang and Meng, *J. Catal.* 142 (1993) 37

➤ Semi-direct dimerisation



Yang and Meng, *J. Catal.* 142 (1993) 37

Ethanol condensation mechanism over Mg_xAlO_y

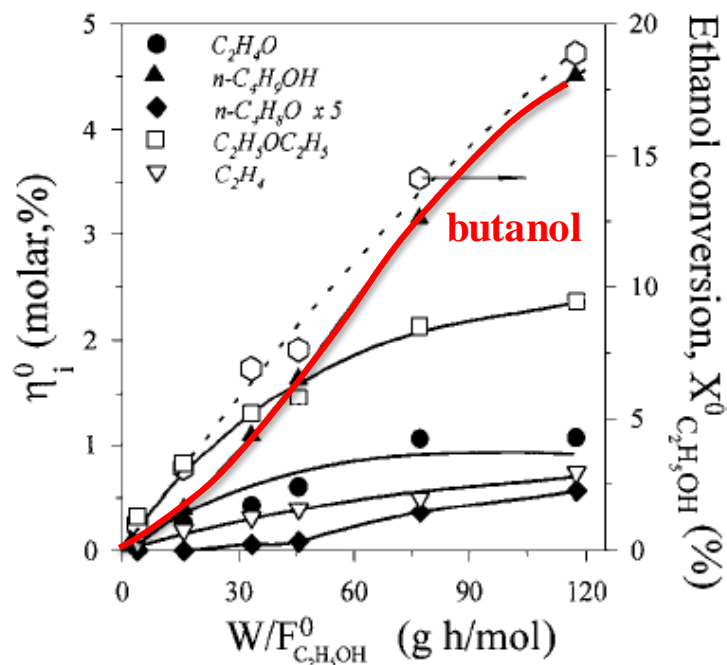
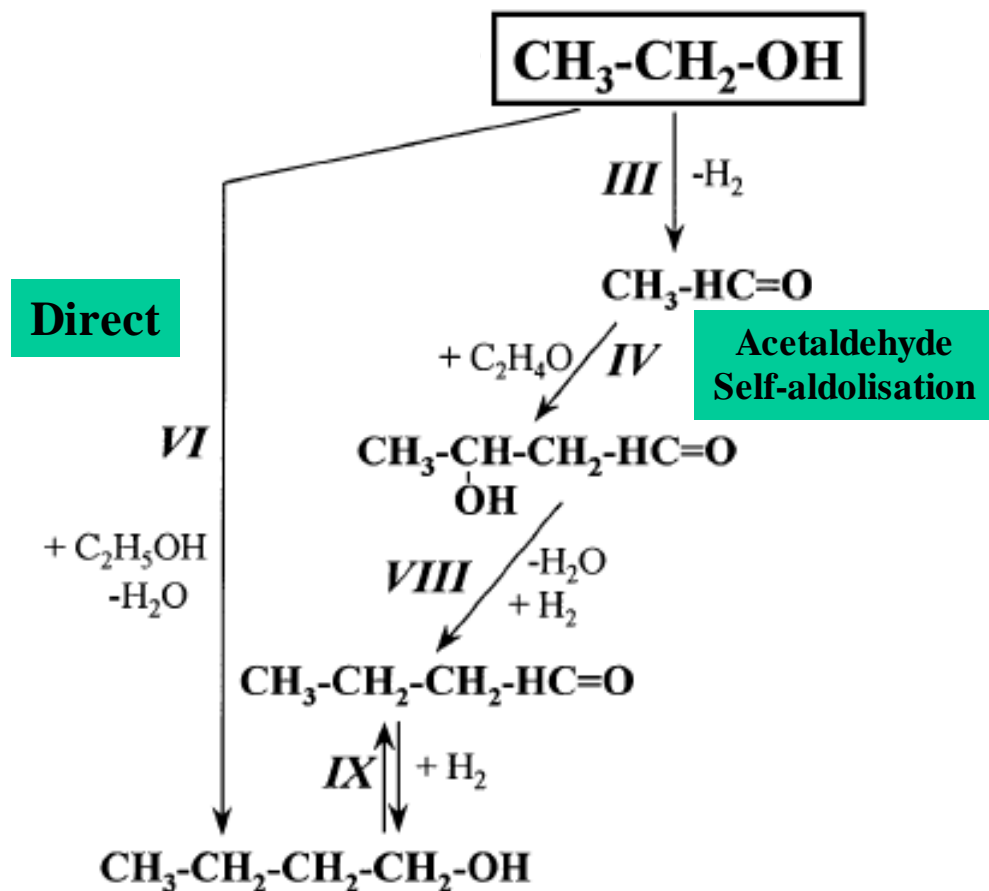


FIG. 5. Product distribution for ethanol conversion reactions on Mg_1AlO_x . Initial product yields (η_i^0) and ethanol conversion ($X_{C_2H_5OH}^0$) as a function of contact time [573 K, 101.3 kPa total pressure].



Di Cosimo, Apesteguia, Gines, Iglesia
 J. Catal. 190 (2000) 261

Outline:

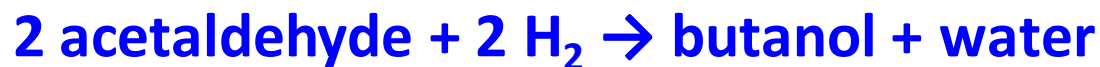
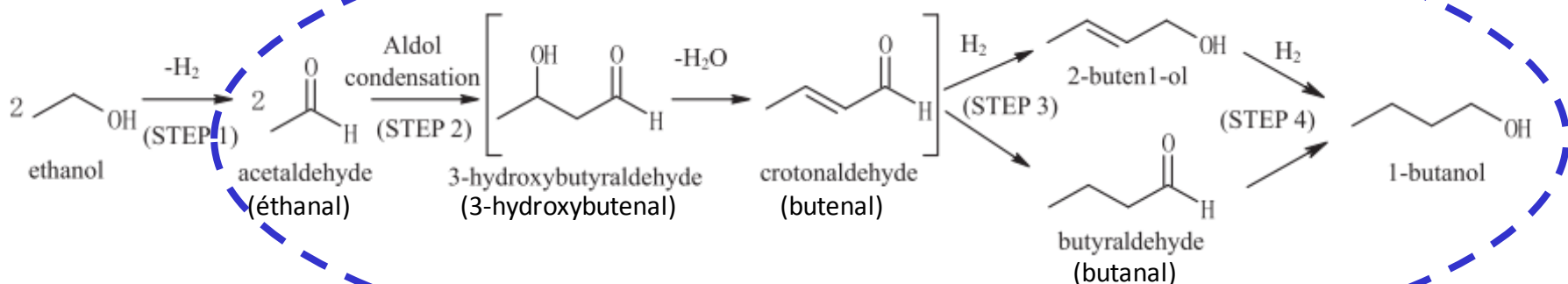
1. Why studying ethanol condensation to butanol?
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Molar Gibbs energy of reaction: $\Delta_r G = \Delta_r G^\ominus + RT \ln Q = RT \ln Q/K$

where $Q =$ reaction quotient

and $K =$ equilibrium constant

HSC Chemistry 6



$$Q = \frac{P_{\text{butanol}} P_{\text{water}}}{(P_{\text{acetaldehyde}} P_{\text{H}_2})^2}$$

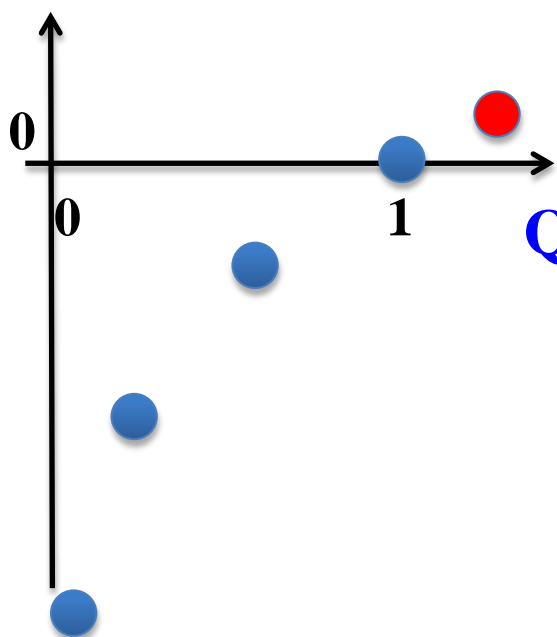
Calculating Q requires quantifying: butanol, acetaldehyde, **H_2O and H_2**

$$Q = \frac{P_{\text{butanol}} P_{\text{water}}}{(P_{\text{acetaldehyde}} P_{\text{H}_2})^2}$$

During a catalytic test,

Q goes from a value of 0 to K or less, but **not higher**

$$\Delta_r G(T) = RT \ln Q/K$$



$Q/K = \eta = \text{progress to equilibrium}$

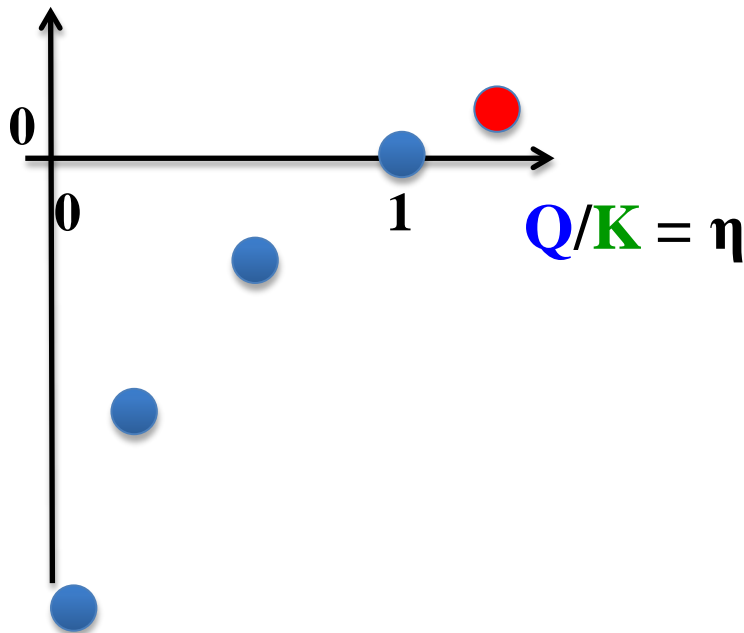
Mechanism validity criterion: $Q/K = \eta \leq 1$

$$Q = \frac{P_{\text{butanol}} P_{\text{water}}}{(P_{\text{acetaldehyde}} P_{\text{H}_2})^2}$$

During a catalytic test,

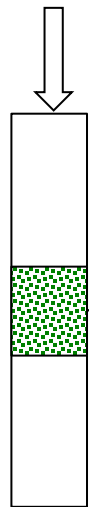
Q goes from a value of 0 to K or less, but **not higher**

$$\Delta_r G(T) = RT \ln Q/K$$



Mechanism validity criterion: $Q/K = \eta \leq 1$

ethanol



Reactor: quartz plug flow reactor

Catalyst: Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ from Accros

Operating conditions: $350^\circ \text{C} < T < 450^\circ \text{C}$

$3.8 < P_{\text{ethanol}} < 19.1 \text{ kPa}$

$1.4 < \text{WHSV} < 56 \text{ g}_{\text{ethanol}} \text{ g}_{\text{cata}}^{-1} \text{ h}^{-1}$

Gas Chromatograph + Mass Spectrometer + FT-IR gas cell

ethanol

butanol

acetaldehyde

ethene

butenol

butadiene

H_2

acetaldehyde

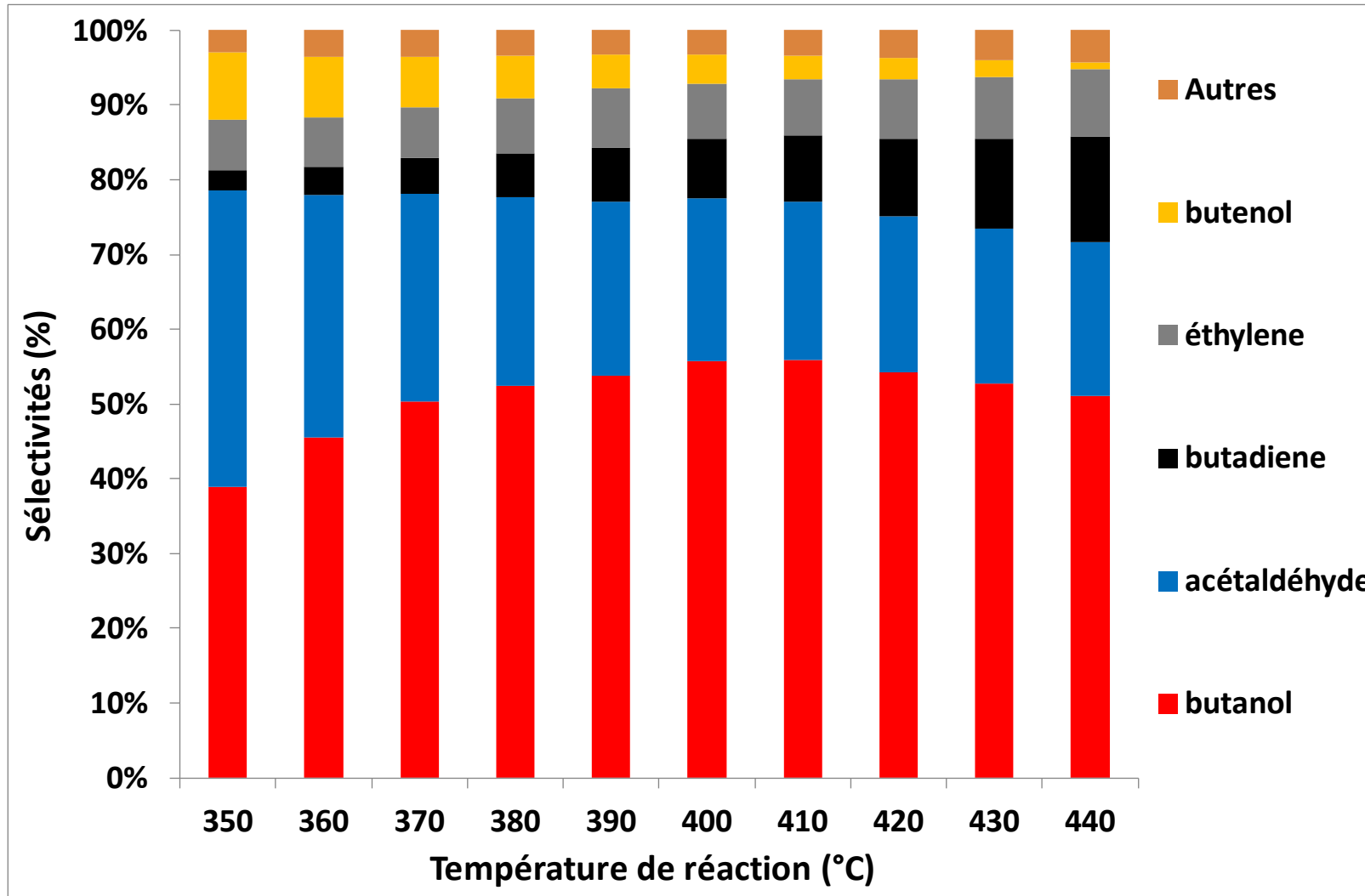
H_2O

Outline:

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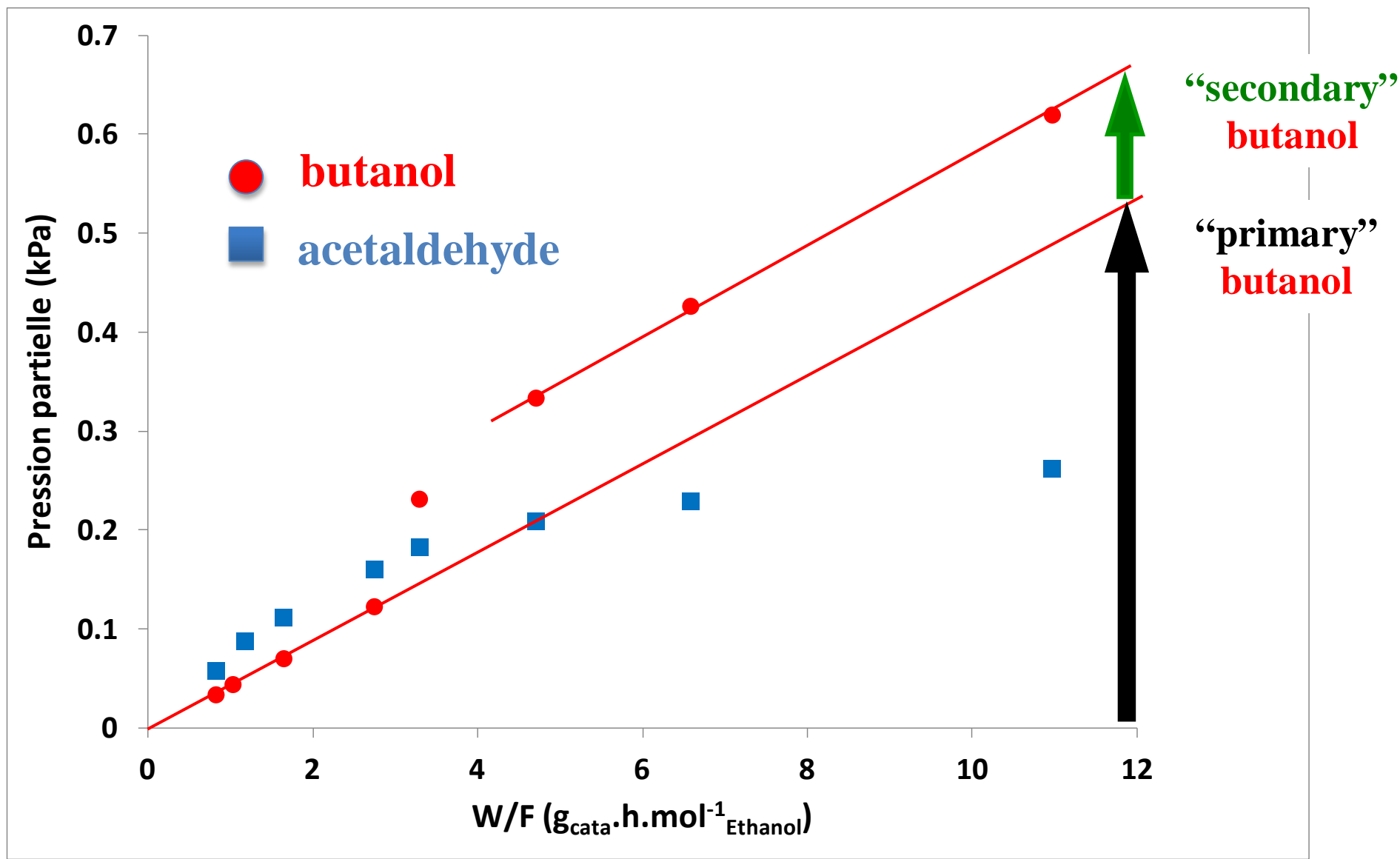
Hydroxyapatite: selectivity vs. temperature

%Ethanol = 15.2 % ; WHSV = 14 h⁻¹



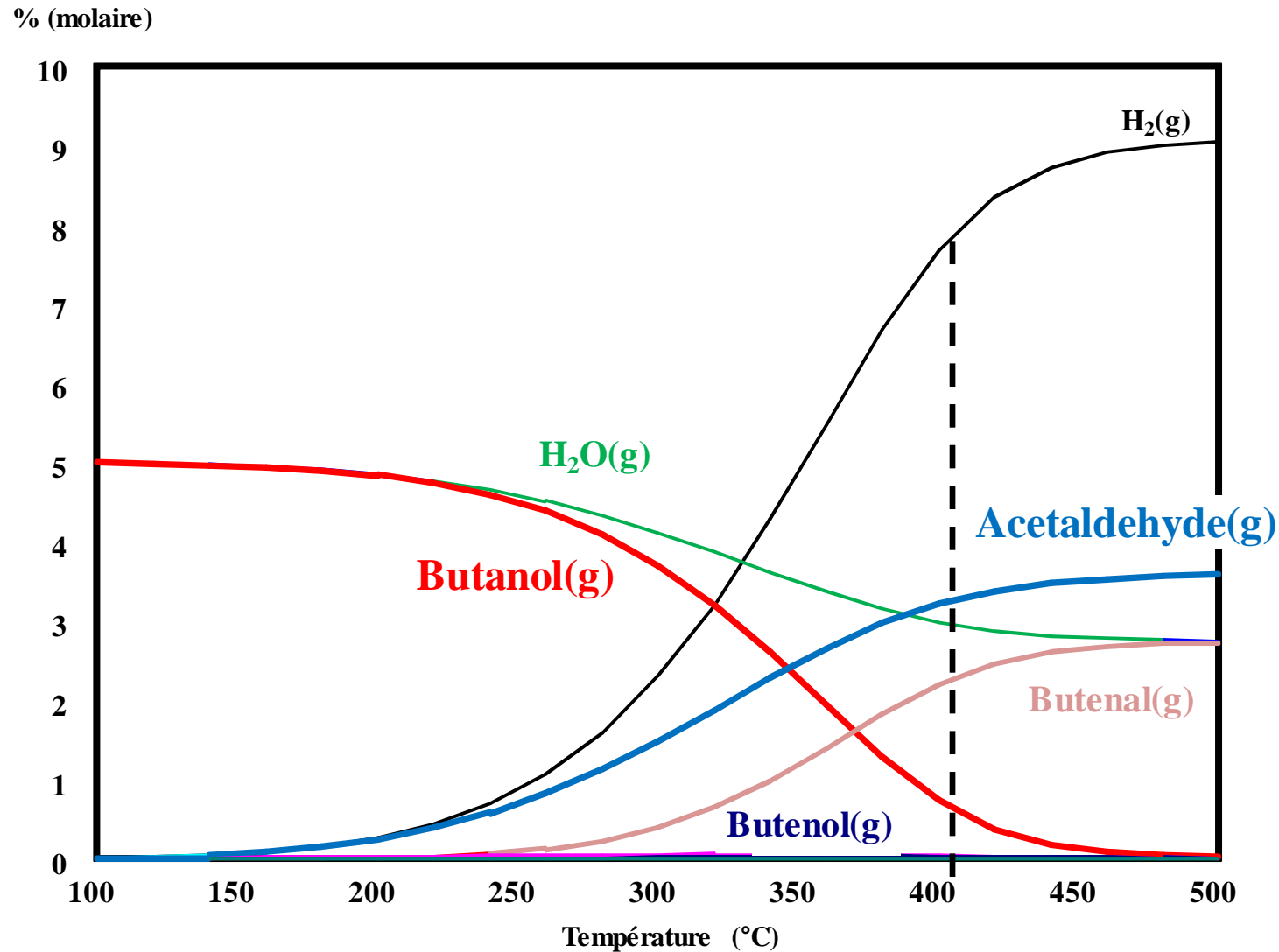
most abundant product is butanol

Effect of contact time at 400 °C



Two routes to butanol? one direct, one involving acetaldehyde?

HSC equilibrium calculation based on self-aldolisation intermediates



At 400°C: acetaldehyde and butenal should be more abundant than butanol

Computing Q/K for:



HSC Chemistry 6

$$Q = \frac{P_{\text{butanol}} P_{\text{water}}}{(P_{\text{acetaldehyde}} P_{\text{H}_2})^2}$$

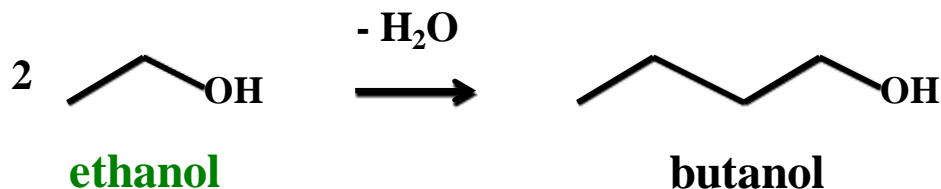
Temperature /°C	%EtOH	WHSV	K	Q	$\eta = Q/K$
350	15,2 %	28 h ⁻¹	546	988231	1807
400	15,2 %	28 h ⁻¹	36	146195	4014
440	15,2 %	28 h ⁻¹	5.5	12150	2225
400	7,6 %	1,4 h ⁻¹	36.4	642553	17644
400	7,6 %	2,1 h ⁻¹	36.4	589451	16186
400	7,6 %	4,2 h ⁻¹	36.4	559582	15366
400	7,6 %	7,0 h ⁻¹	36.4	585985	16091

$$Q/K \gg 1$$

Suggested reaction mechanisms:

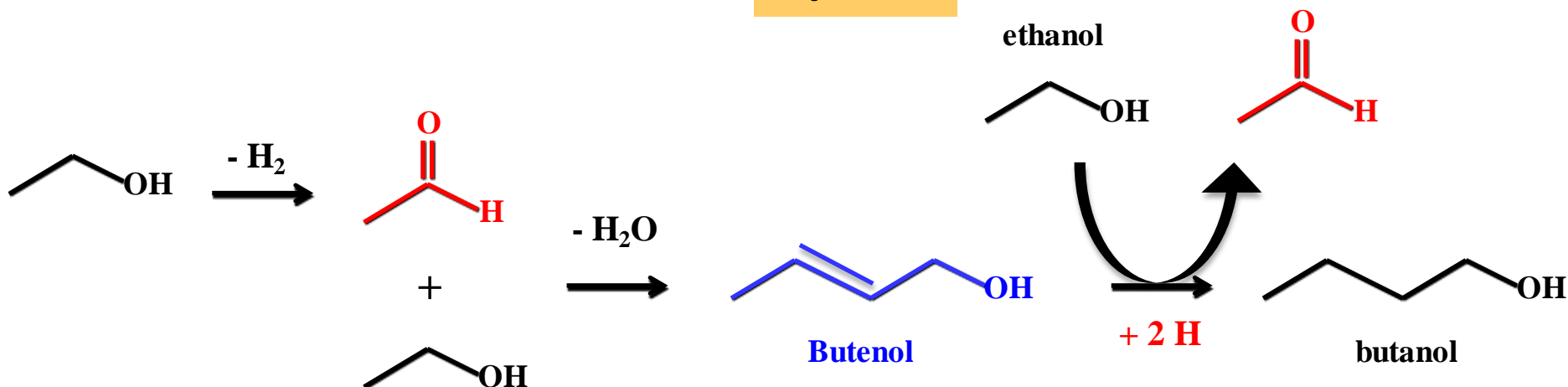
➤ Main: direct reaction mechanism

$Q/K < 1$



➤ Minor: semi-direct reaction mechanism

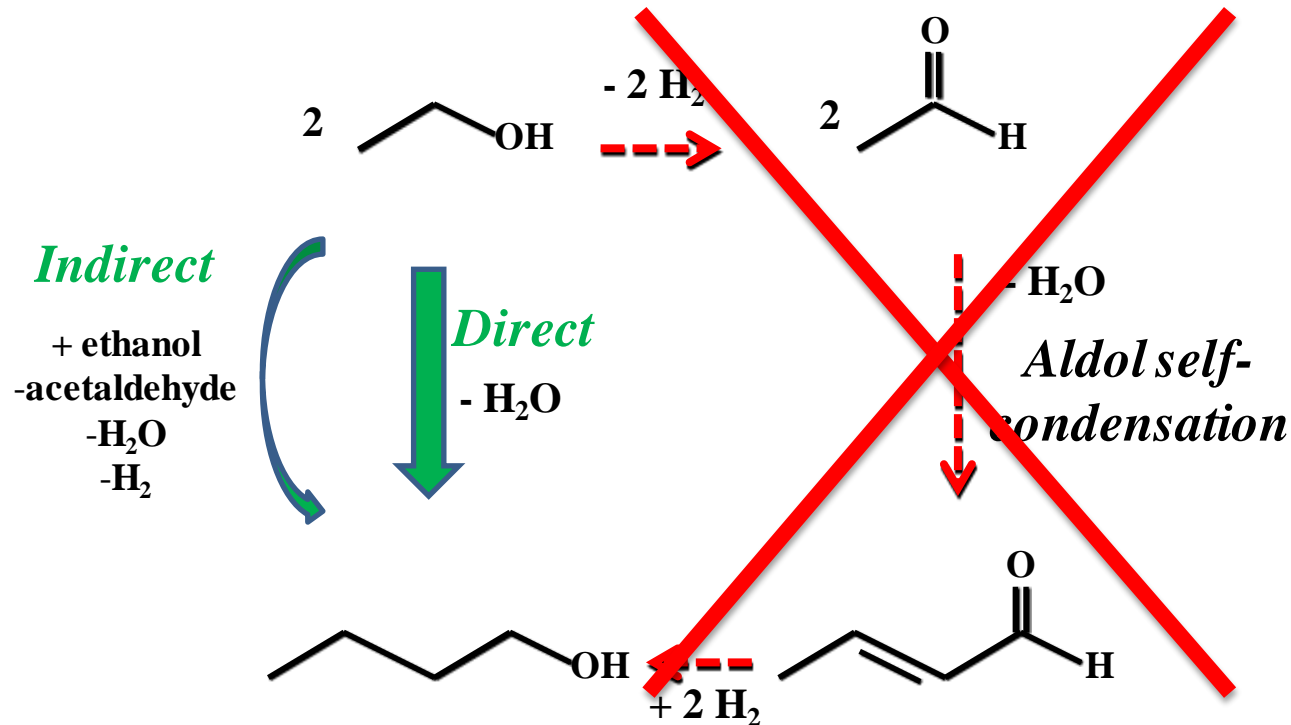
$Q/K < 1$



Final hydrogenation: H-transfer from sacrificial ethanol (not via H_2 dissociation)

Minor route is intrinsically less selective: one ethanol is sacrificed

Conclusion:
ethanol condensation at high T
over hydroxyapatite without metals



Target? try to hinder the less selective mechanism that involves acetaldehyde, contrary to the case of low T metal-promoted reactions!

5. Other cases with useful insight from thermodynamics

n-alkane hydroisomerisation over MoOx:

bifunctional mechanism, RDS is different for C₄ and C₅

Meunier et al., Chem. Commun. 1999, 259

CH₃OH + H₂O = 3 H₂ + CO₂ over Cu/Zn/Zr/Al:

CO not reaction intermediate, secondary reaction product

Meunier, Chem. Commun. 2003, 1954

C₃H₆-SCR of NO over Ag/ γ-Al₂O₃:

NO₂ not formed via NO + O₂, but via C_xH_yN_zO + O₂

Breen et al. , Chem. Commun. 1999, 2247

Alkane hydroisomerisation over reduced MoO₃

Reaction mechanism?

- bifunctional (metallic site + acidic site)

Matsuda et al., Catal. Lett. 47 (1997) 99

- metallacyclobutane

Blekkan et al., Ind. Eng. Chem. Res. 33 (1994) 1657

Experimental details for n-butane to isobutane :

MoO₃ (Fluka), BET < 2 m² g⁻¹

10 % n-butane / H₂

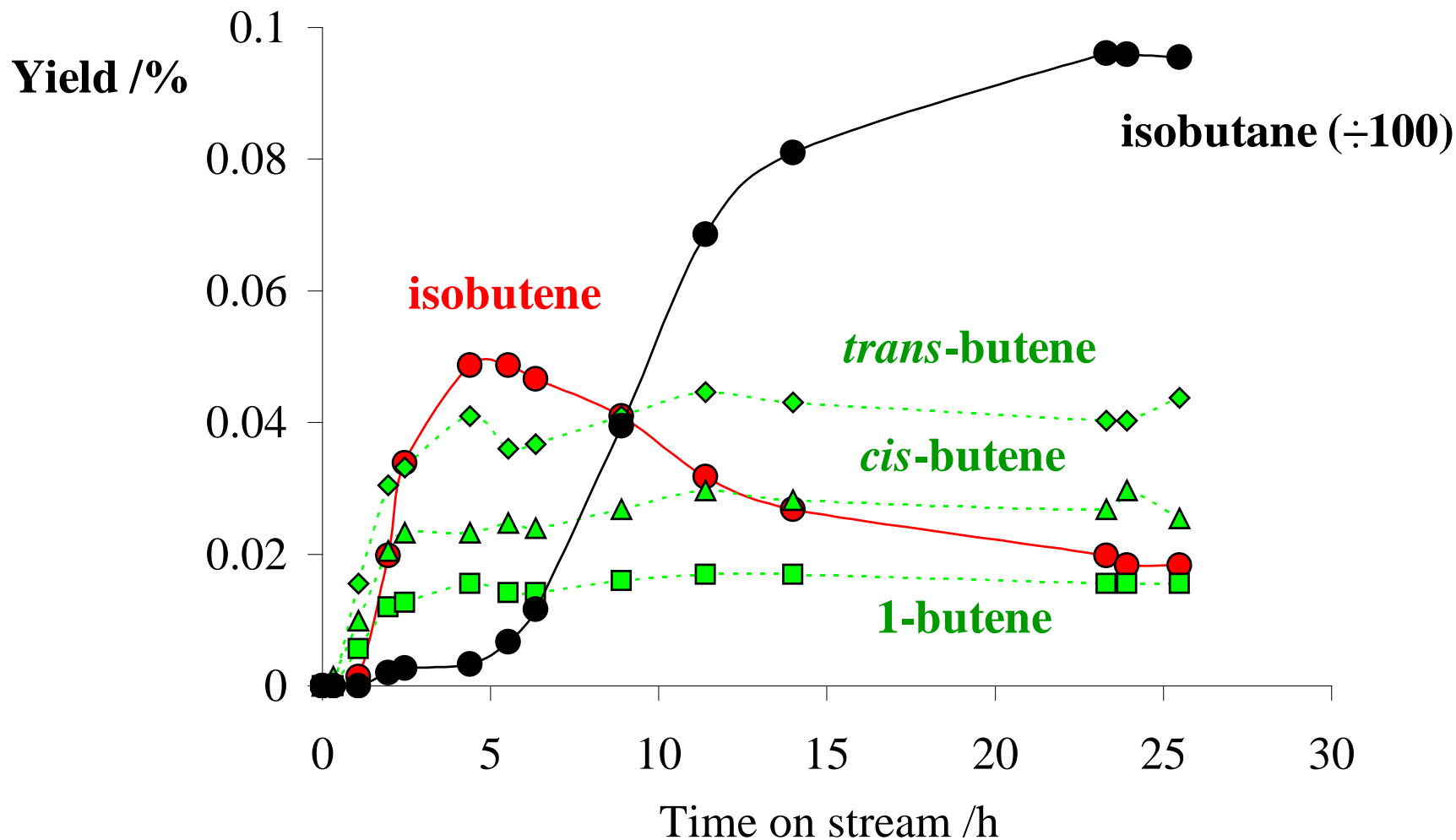
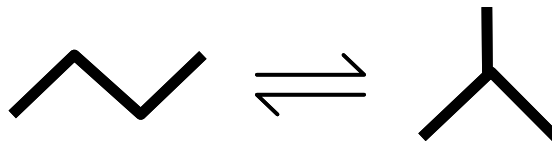
Total flowrate: 20-100 ml min⁻¹

Mass of catalyst: 20-500 mg

T = 350°C (623 K)

Case 1: n-Alkane hydroisomerisation

n-butane hydroisomerisation on MoO₃



Case 1: n-Alkane hydroisomerisation

De/hydrogenation steps



	1h	2h	6h	Steady-state	Thermodynamic ratio
<u>n-butane</u> 1-butene	16000	8300	7000	6000 ± 800	6600
<u>isobutane</u> isobutene	0.045	10	17	500 ± 80	470

De/hydrogenation rates increases with TOS towards equilibrium

Case 1: n-Alkane hydroisomerisation

Skeletal isomerisation steps



1h

2h

6h

Steady-state

**Thermodynamic
ratio**

$6 \cdot 10^{-7}$

$1.8 \cdot 10^{-4}$

$8.3 \cdot 10^{-3}$

0.11 ± 0.1

0.58

isobutane

n-butane

isobutene

1-butene

0.27

1.63

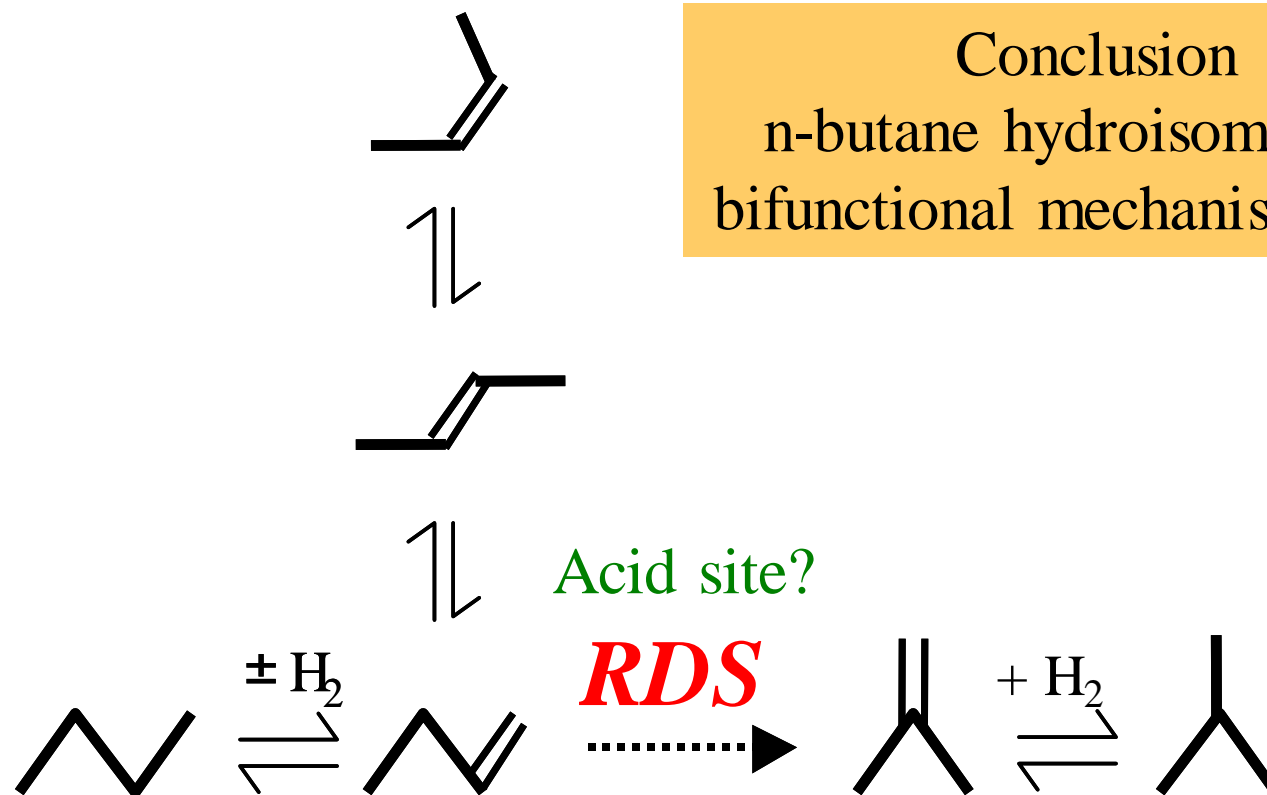
3.3

1.2 ± 0.2

8.12

Skeletal isomerisation rate gradually increases, not at equilibrium:
it is the rate-determining step (RDS)

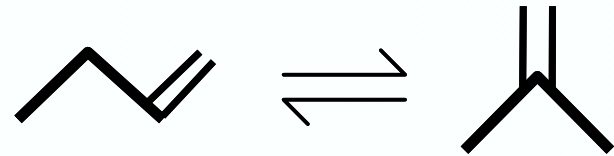
Case 1: n-Alkane hydroisomerisation



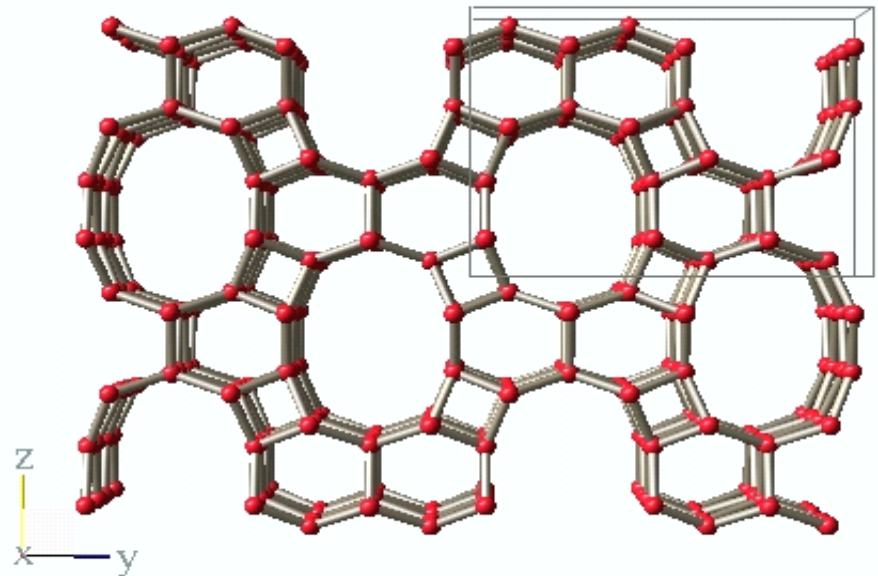
Conclusion 1:
n-butane hydroisomerisation:
bifunctional mechanism operates

Reduced MoO₃

*Can the activity be promoted by a
n-alkene isomerisation catalyst?*

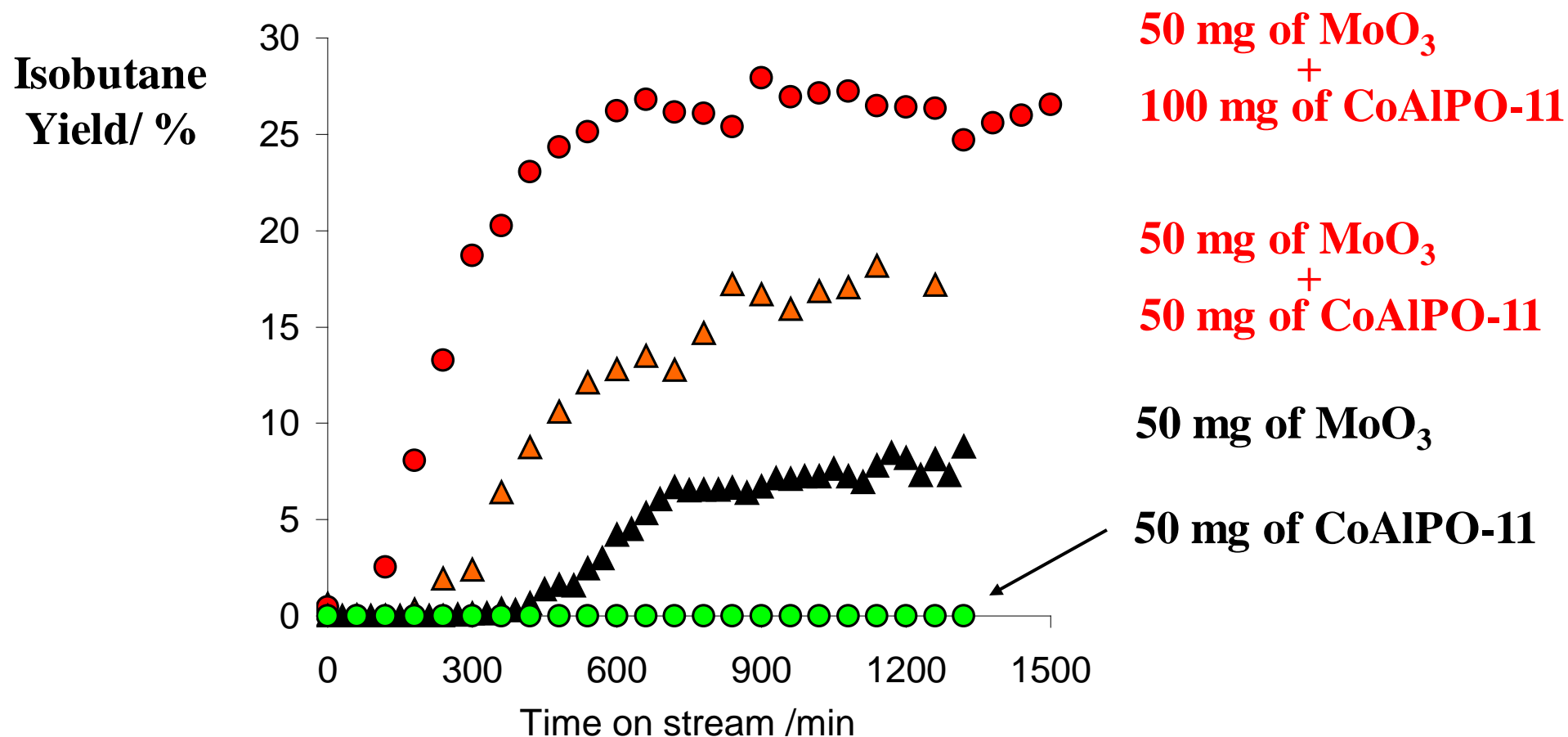


CoAlPO-11 (AEL structure)
monodimensional
10-member ring framework
[001] 4.5 nm x 6.5 nm



Case 1: n-Alkane hydroisomerisation

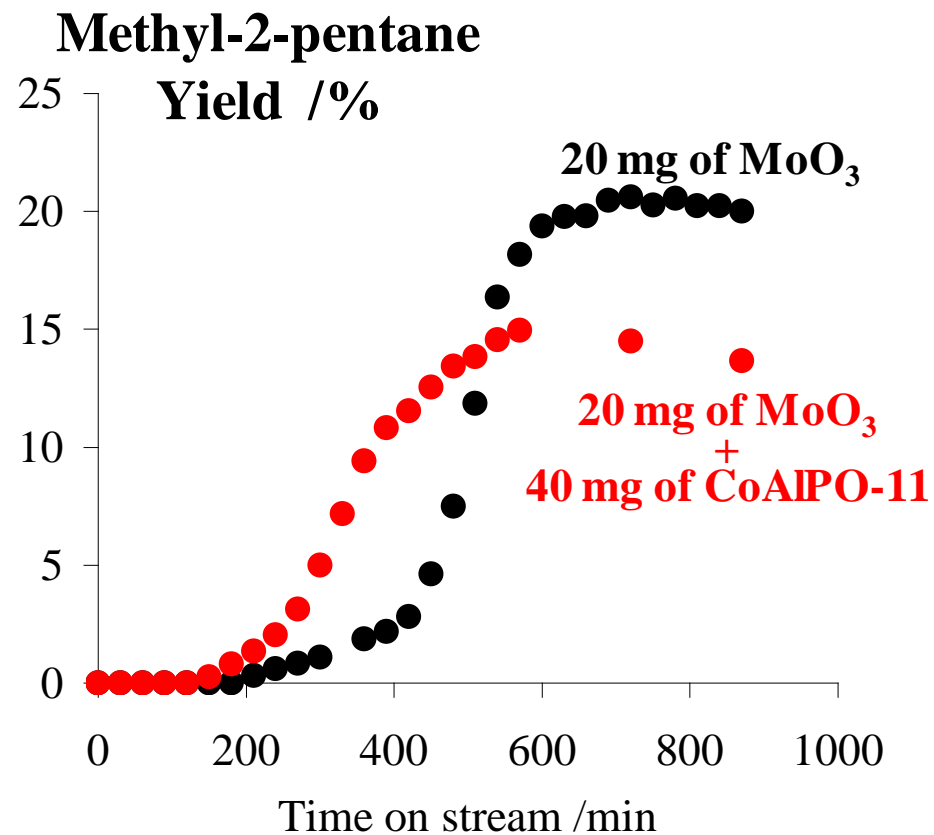
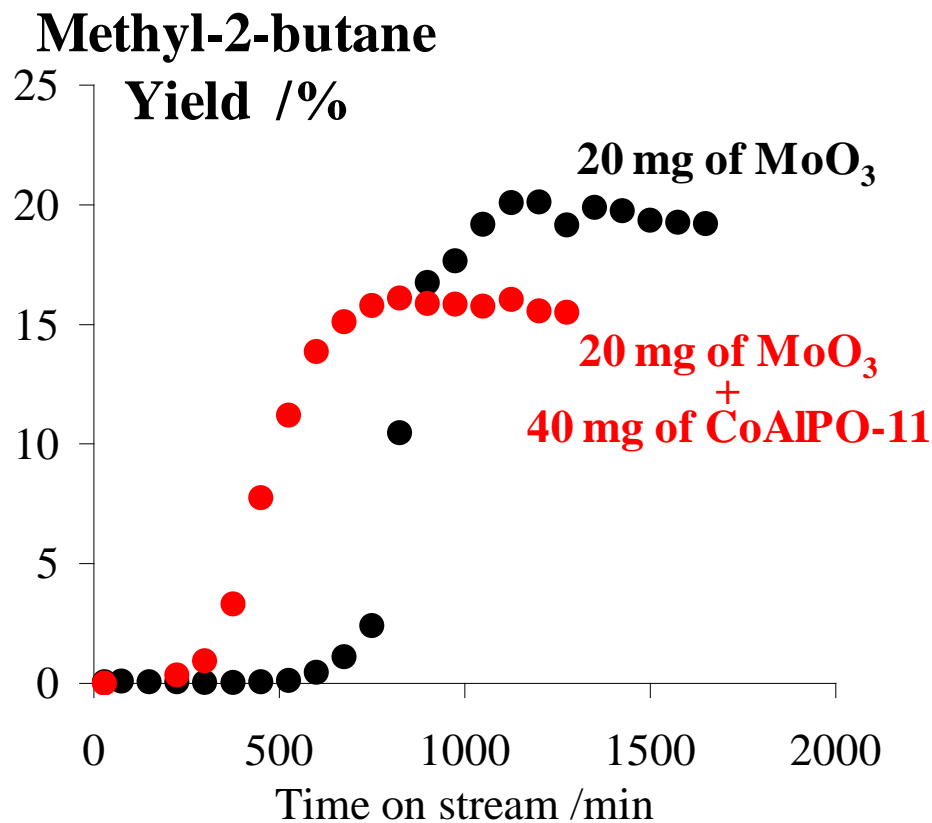
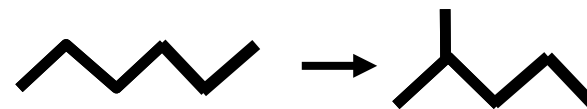
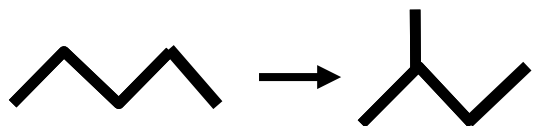
n-butane hydroisomerisation: promotion by CoAlPO-11?



CoAlPO-11 promotes MoO₃ for n-butane hydroisomerisation

Case 1: n-Alkane hydroisomerisation

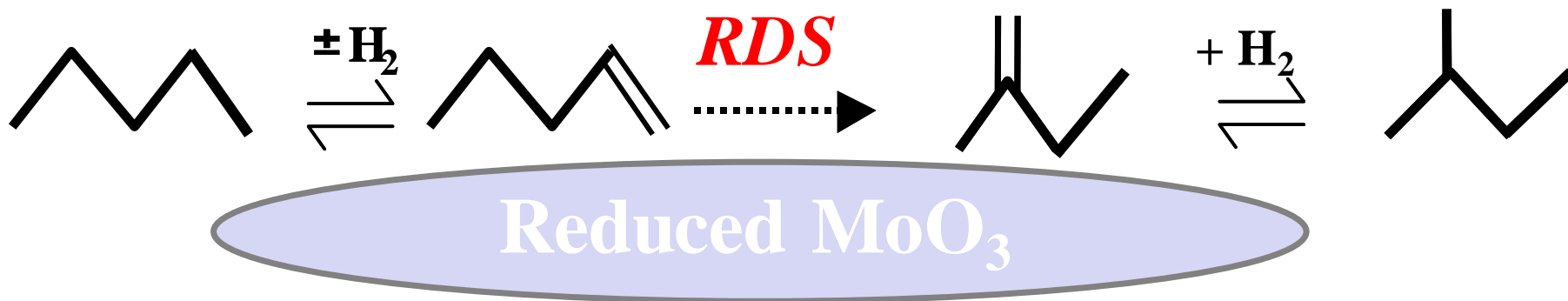
nC5 and nC6 hydroisomerisation/MoO₃: promotion by CoAlPO-11?



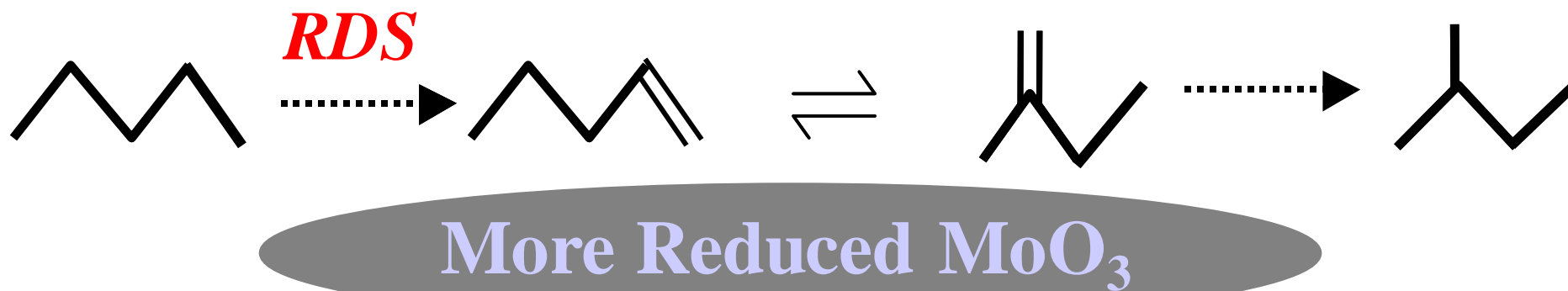
CoAlPO-11: - Initially promotes nC₅₊ to iC₅
- At steady-state: small inhibition

Case 1: n-Alkane hydroisomerisation

Short TOS



Steady-state



Conclusion 2: nC5 and nC6 hydroisomerisation:
RDS limited by de/hydrogenation steps at steady-state

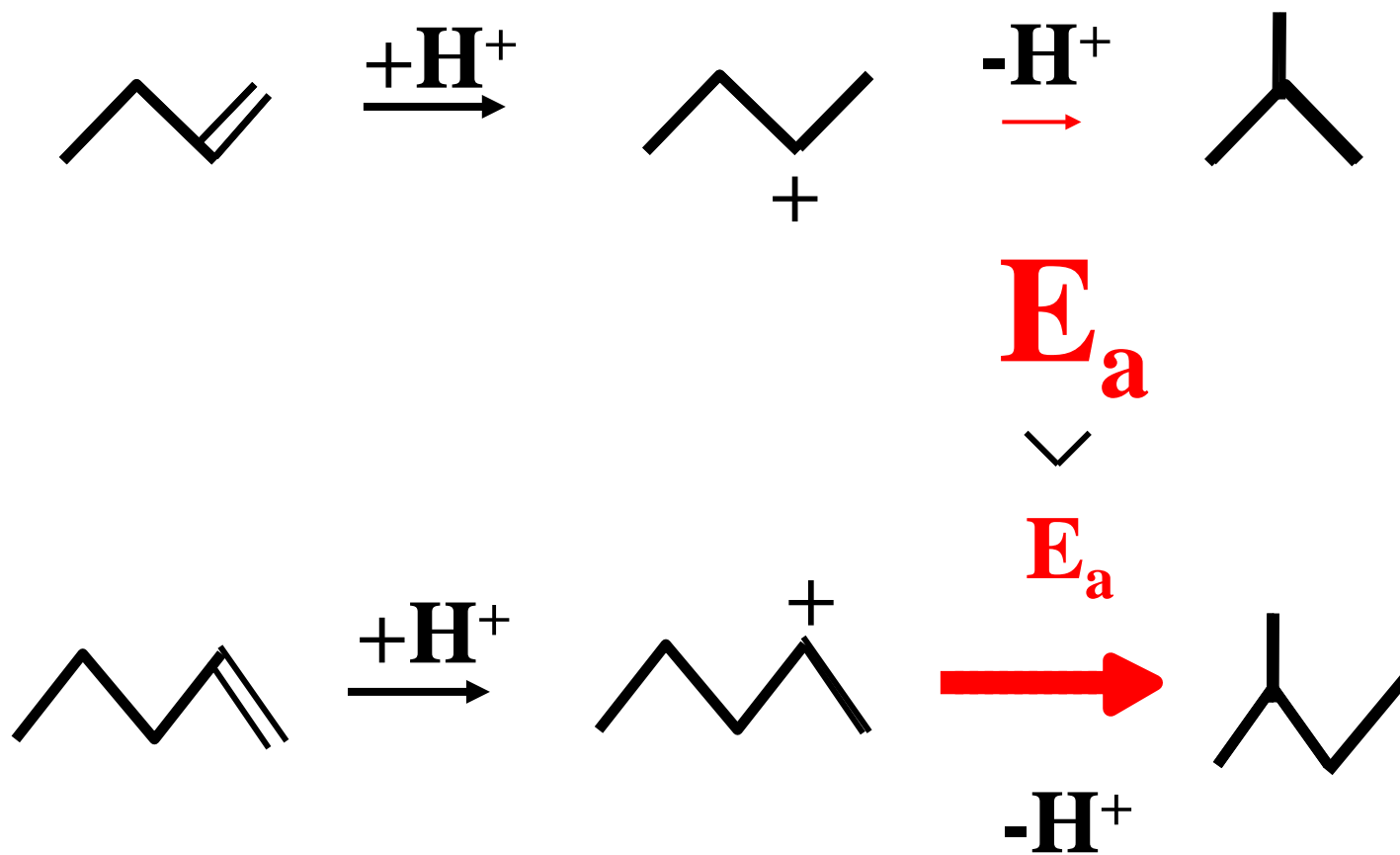
Meunier et al., Catal. Today, 2006, 112, 64

Case 1: n-Alkane hydroisomerisation

Why C₄ and C₅₊ hydroisomerisation RDS are different?

DFT calculation on energetics of branching of carbenium ions

M. Boronat et al., Appl. Catal. A: Gen. 146 (1996) 207



Other examples:

1. n-alkane hydroisomerisation

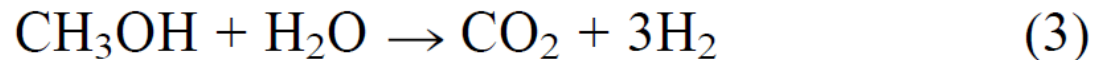
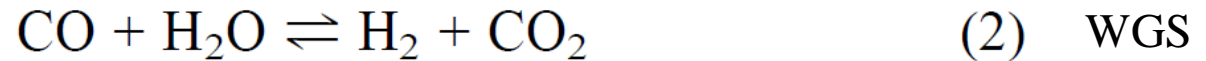
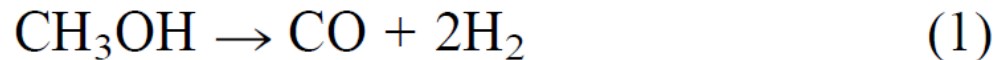
2. Methanol steam reforming

3. NO oxidation to NO₂ during SCR

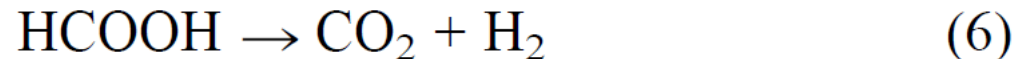
methanol steam reforming:



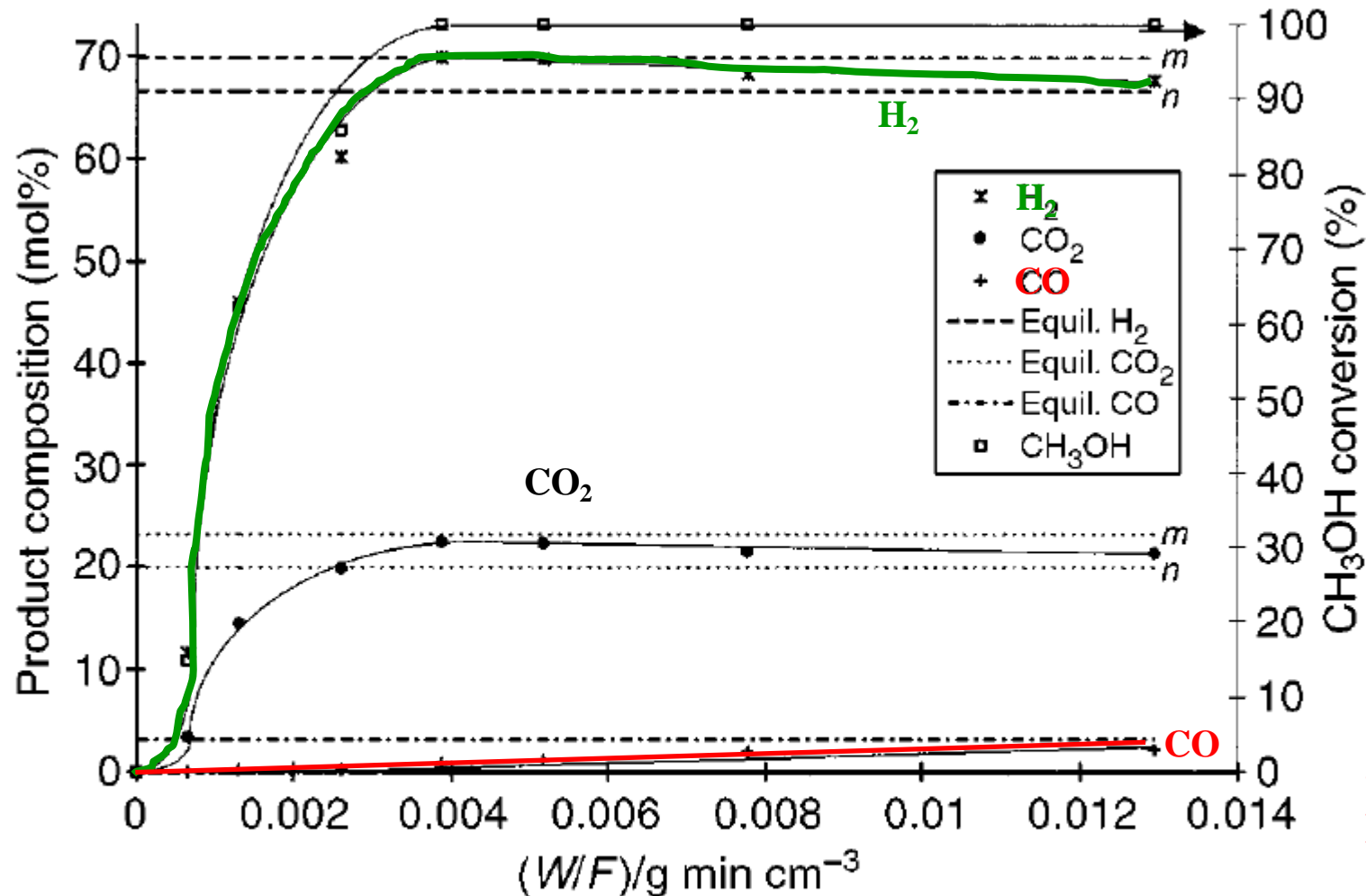
Mechanism based on CO as reaction intermediates:



Other mechanisms not based on CO have been proposed, e.g.:



Case 2: Methanol steam reforming



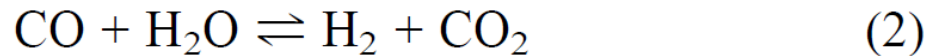
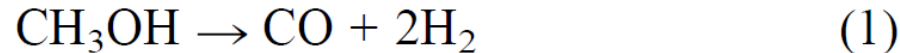
CO: seems to be a secondary product

Fig. 1 The influence of W/F on the product compositions at $T = 300\text{ }^{\circ}\text{C}$ over a $\text{CuO}/\text{ZnO}/\text{ZrO}_2/\text{Al}_2\text{O}_3$ catalyst, $m =$ equilibrium excluding CO from calculations, $n =$ equilibrium including CO in calculations ($\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1.3$, $P = 101\text{ kPa}$).

If CO included in equilibrium calculation (lines n),
H₂ and CO₂ concentrations go beyond equilibrium values!

Case 2: Methanol steam reforming

Because the proportion of H₂ and CO₂ observed exceeds that predicted in the **CH₃OH/H₂O/H₂/CO₂/CO** system, this system is not relevant.



(1) + (2) cannot be the primary reaction pathway,
another reaction scheme (unknown) applies

Only at higher contact time does the proportions of CO, H₂ and CO₂ in the **CH₃OH/H₂O/H₂/CO₂/CO** system becomes consistent with that predicted by the thermodynamics: this is because the **reverse WGS** reaction is now significant.

CO is formed consecutively from CO₂

Importance of selecting the set of species relevant
to the reaction scheme

Other examples:

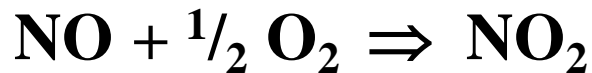
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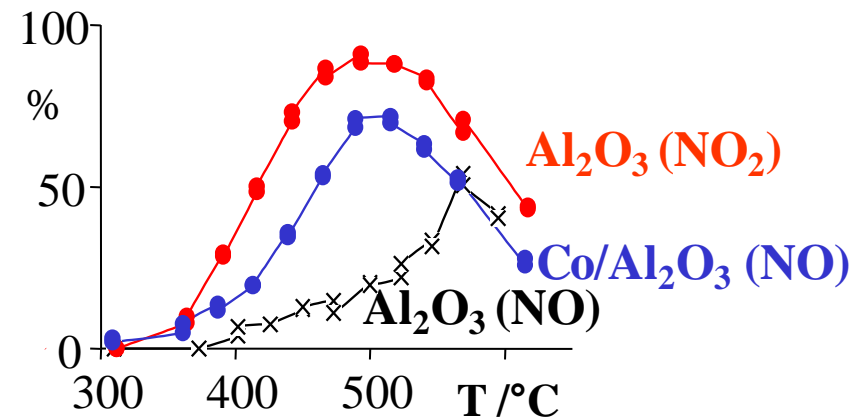
C_xH_y-SCR of NO over Al₂O₃-based catalysts

Role of CoO_x in CoO_x / γ-Al₂O₃



H. Hamada et al., Catal. Today 29 (1996) 53

N₂ yield during the C₃H₆-SCR of NO_x



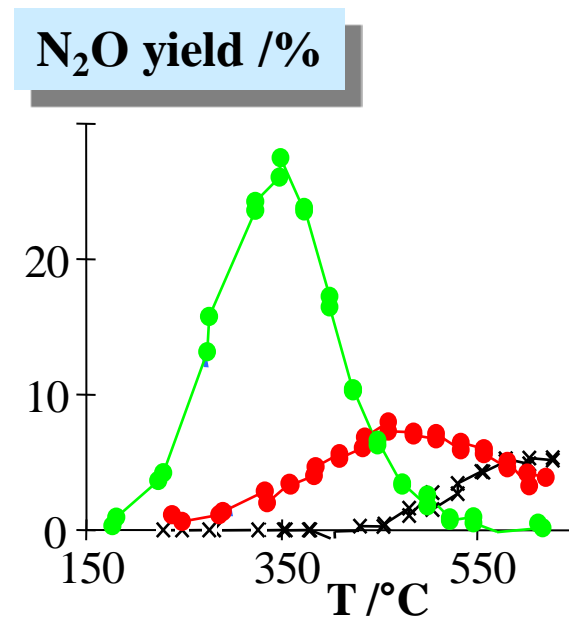
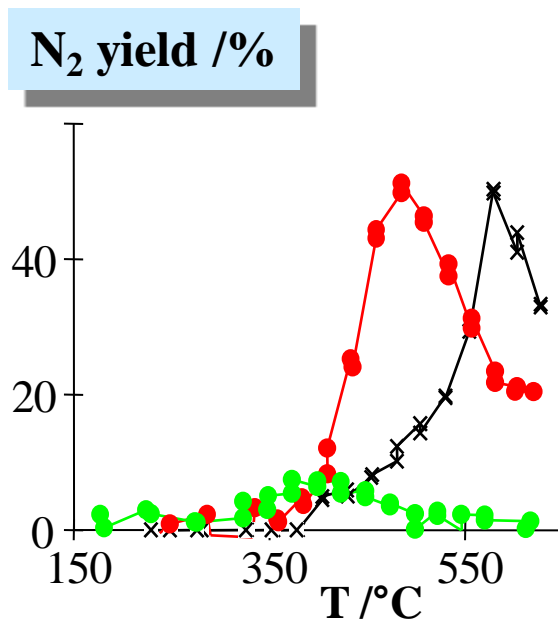
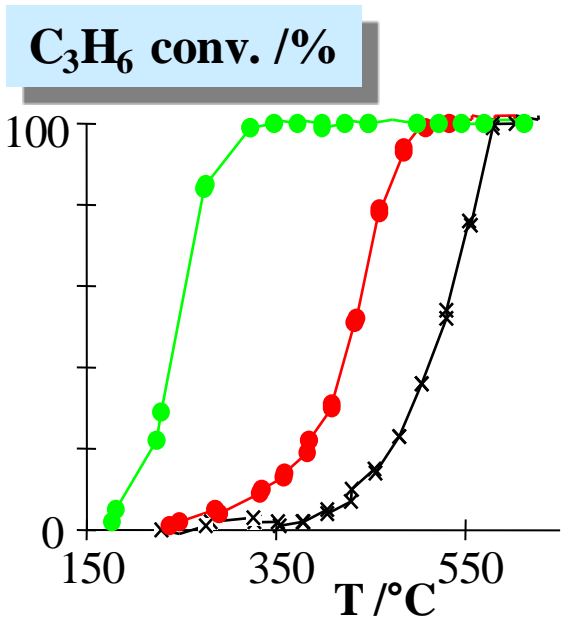
Yet NO + O₂ to NO₂ activity low!

J. Yan et al., J. Catal. 172 (1997) 178

Is NO + O₂ to NO₂ really important?

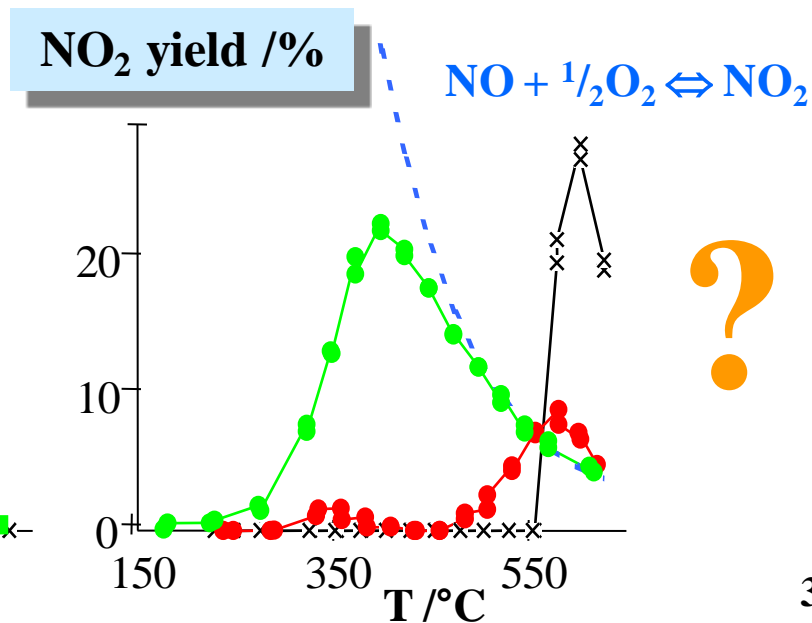
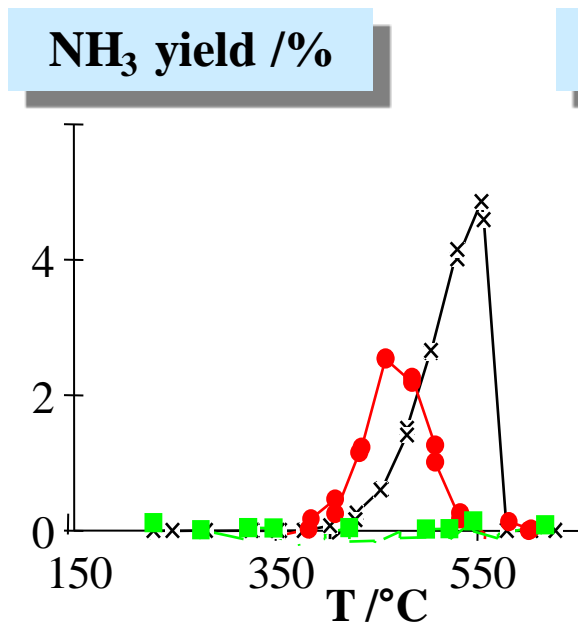
Case 3: NO oxidation to NO₂ during SCR

C₃H₆-SCR of NO over Ag/ γ -Al₂O₃



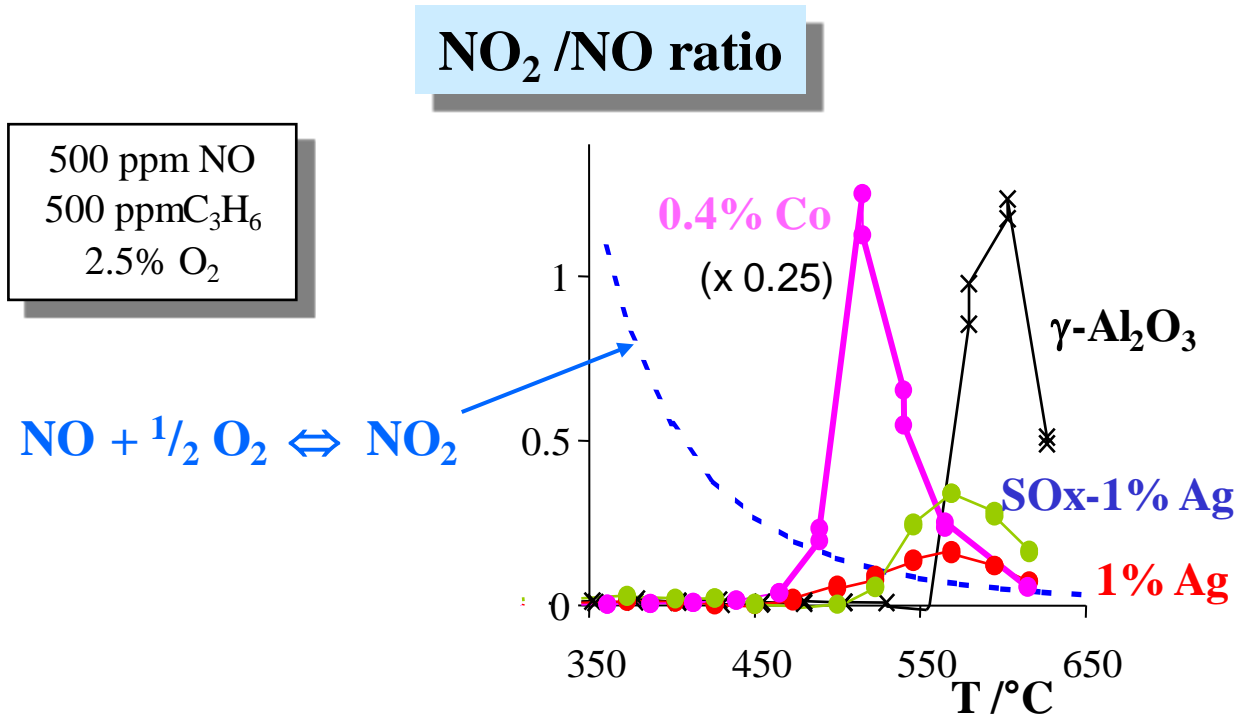
10% Ag / Al₂O₃
1% Ag / Al₂O₃
Al₂O₃

500 ppm NO
 500 ppm C₃H₆
 2.5% O₂
 W/F = 0.06 g s cm⁻³



Case 3: NO oxidation to NO₂ during SCR

NO₂ formation over γ -Al₂O₃-based catalysts



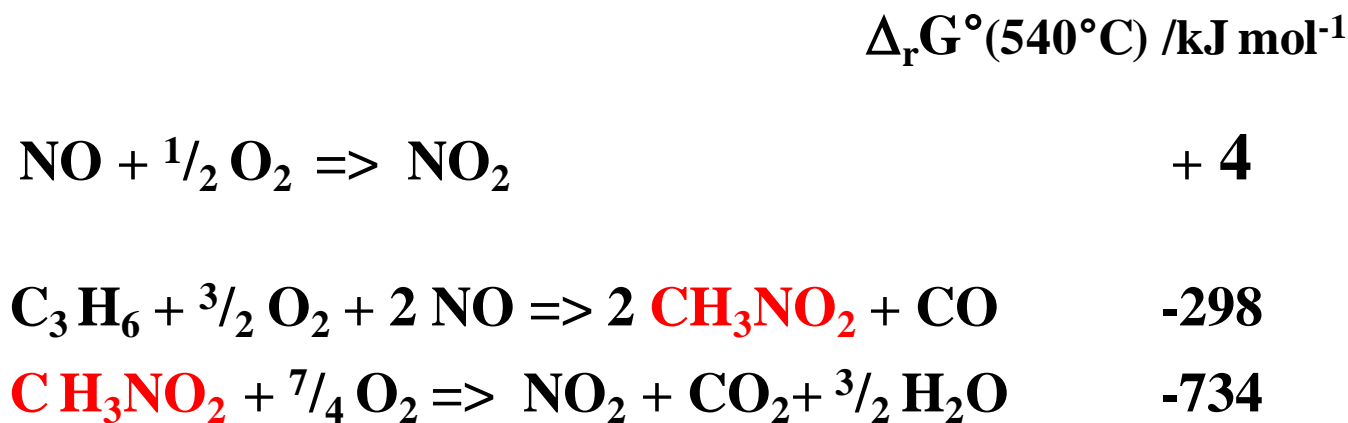
The system to consider is **not** NO, O₂ and NO₂

Case 3: NO oxidation to NO₂ during SCR

Origin of the NO₂ formation over γ -Al₂O₃-based catalysts

Homogeneous oxidation of alkanes:
formation of R-NO₂, role of R-ONO

K. Otsuka et al., Catal. Today 45 (1998) 23

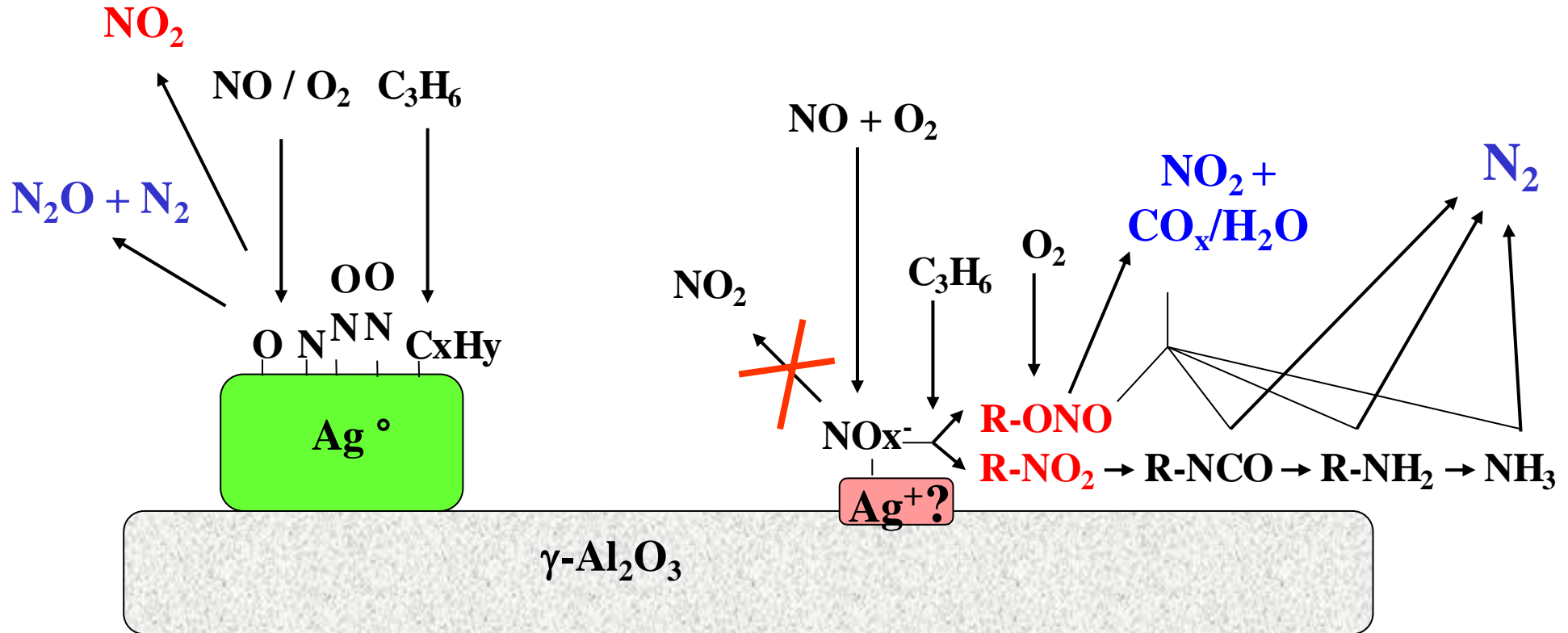


F.C. Meunier et al., Chem. Commun. (1999) 259

The true R-NO_x intermediate(s) is(are) likely more complex, but these calculi show that such routes afford high concentration of NO₂, contrary to the direct oxidation.

Case 3: NO oxidation to NO₂ during SCR

Suggested mechanisms of the
C₃H₆-SCR of NO over **high** and **low** Ag loading γ -Al₂O₃



Meunier et al. J. Catal. 187 (1999) 493.

Conclusion: *Kinetics and Thermodynamics*

The comparison of the **reaction quotient (Q)** or similar ratios to the corresponding **thermodynamic equilibrium ratios (e.g. K)** can be very useful in supporting or rejecting a reaction mechanism.