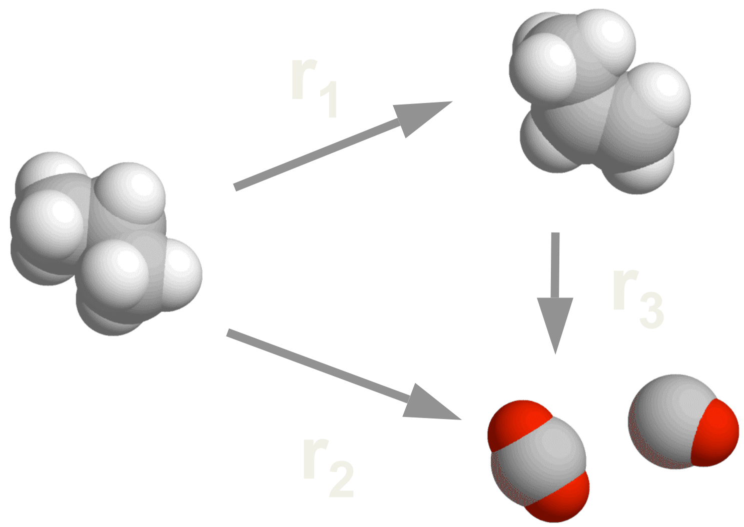
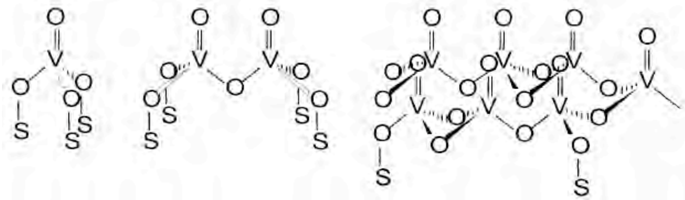
A critical review of kinetic studies of ODP at catalysts with different support materials

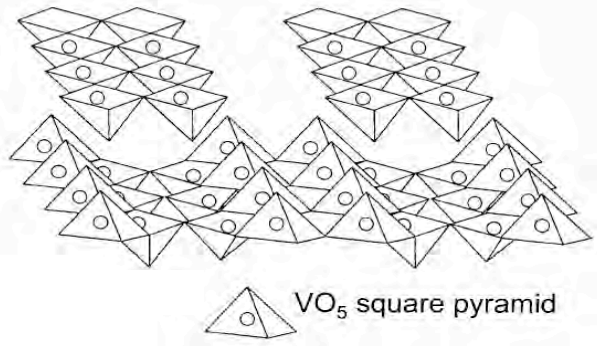
Carlos Carrero, Arne Dinse, Olga Ovsitser,
Evgenii Kondratenko, Reinhard Schomäcker



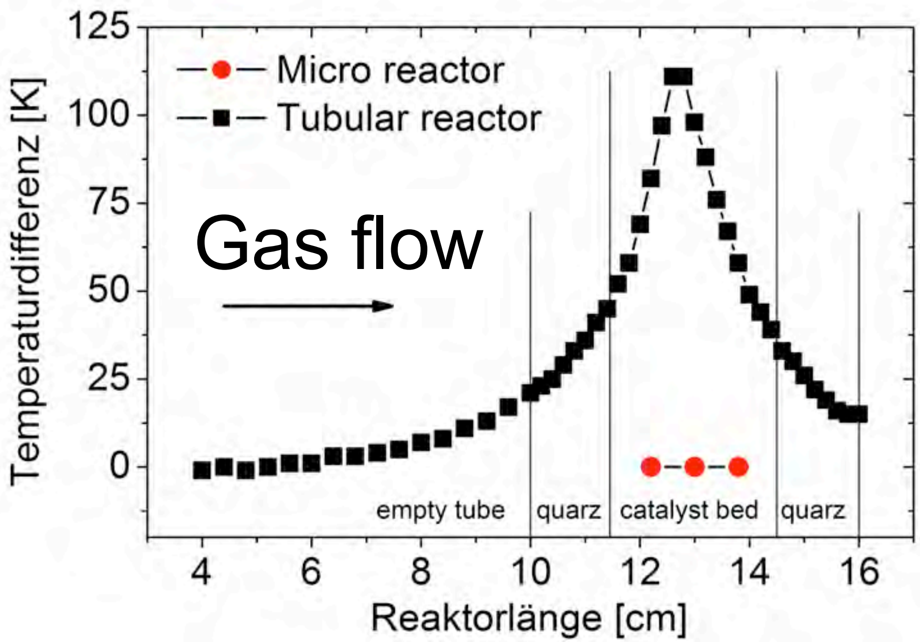
Suppo rt	Ea (KJ/mo	TOF (*10^{-3} S^{-1})	Temp. (°C)	BET (g/m^2)	V_2O_5 (%wt)	V (atom/nm^2	Study
SiO_2	103	-	400 - 500	600	2,7	0,7	Dinse, J Mol Catal 307 (2009) 43
SiO_2	146	1,3 (400°C)	400 - 500	151	0,6	0,3	Dinse, J Mol Catal 289 (2008) 28
SiO_2	-	15 (475°C)	400 - 500	227 - 892	0,6 – 5,3	0,08 – 1,38	Kondratenko, Catalysis Today 112 (2006) 60
SiO_2	100	-	425 - 525	281	5	2,1	Puglisi, Catalysis Letters 41 (1996)
SiO_2	106	2 – 10	425 - 525	311 - 746	1,1 – 8,2	0,15 – 3,11	Karakoulia, Catalysis Today 141
SiO_2	-	2,5 - 3	450 - 475	790 - 1059	0,2 – 5,3	0,5 - 5	Kondratenko, Journal of Catalysis 234
SiO_2	97 – 51	6 - 13	400 - 500	380 – 643	1,9 - 13	0,2 – 7,6	Carrero/Schomäcker “in
SiO_2	63 – 86	-	460 - 520	117	28,4	15	Grabowski, Chem Eng Proc 54 (2004)
SiO_2	-	10 – 20	500	300 –	2,7 – 11	0,4 – 25,4	Ovsitzer J Phys Chem C 111 (2007)
TiO_2	54	-	350 –	-	4	6,6	Routray Applied Catalysis A 265
TiO_2	65 – 73	-	340 –	-	1 – 3	1,4 – 4,6	Shee Catalysis Today 118
TiO_2	56	-	400 –	66	1,6	1,5	Dinse J Mol Catal 289 (2008) 28
Al_2O_3	96	6,8 (400°C)	400 –	108	2,1	1,4	Dinse J Mol Catal 289 (2008) 28
Al_2O_3	115 -120	-	330 -390	-	2 – 30	1,4 – 34,2	Argyle, Journal Catalysis 208
Al_2O_3	113	-	400 –	88 – 100	0,7 – 15	0,5 - 11,1	Dinse, J Mol Catal 289 (2008) 28
Al_2O_3	81	-	350 -500	-	10	4,5	Shee, Applied Catalysis A 265 (2004)
Al_2O_3	-	2 – 30	-	86 – 100	-	0,5 – 7,7	Chen, Journal of Catalysis 209
ZrO_2	78	56 (400°C)	400 –	108	1,6	1	Dinse, J Mol Catal 289 (2008) 28
ZrO_2	99	-	400 -500	-	10	3,9	Chen, J Phys Chem 104 (2000)
ZrO_2	92 – 96	-	340 –	-	-	4,5	Piek, Journal Catalysis 224
ZrO_2	-	2,3 – 3	400 –	180 -340	0 – 30	0,8	Khodakov, Journal Catalysis 117
ZrO_2	-	10 – 70	430	144 - 160	2 – 30	0,9 – 6,2	Chen, Journal Catalysis 209 (2002)

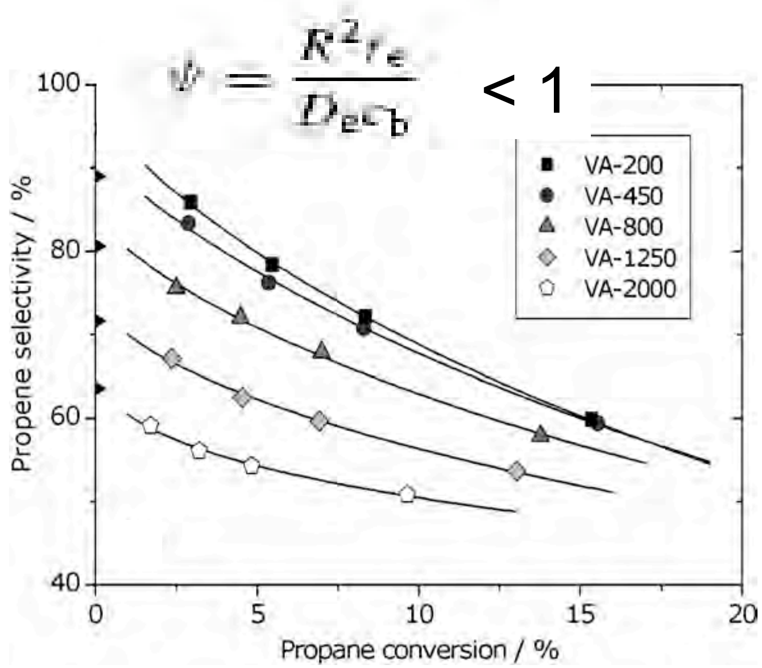
Reasons for variations in kinetic data:





- Different catalytic species
- Hot spots
- Mass transfer linitations





$VO_x/\gamma\text{-}Al_2O_3$, d_p = 0,2–2 mm, 1 bar,
500 °C, $C_3H_8/O_2/N_2$ = 29,1/14,5/56,4

Suppo rt	Ea (KJ/mo	TOF (*10^{-3} s^{-1})	Temp. (°C)	BET (g/m^2)	V_2O_5 (%wt)	V ($atom/nm^2$)	Study
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SiO_2	-	15 (475°C)	400 - 500	227 - 892	0,6 – 5,3	0,08 – 1,38	Kondratenko, Catalysis Today 112 (2006)
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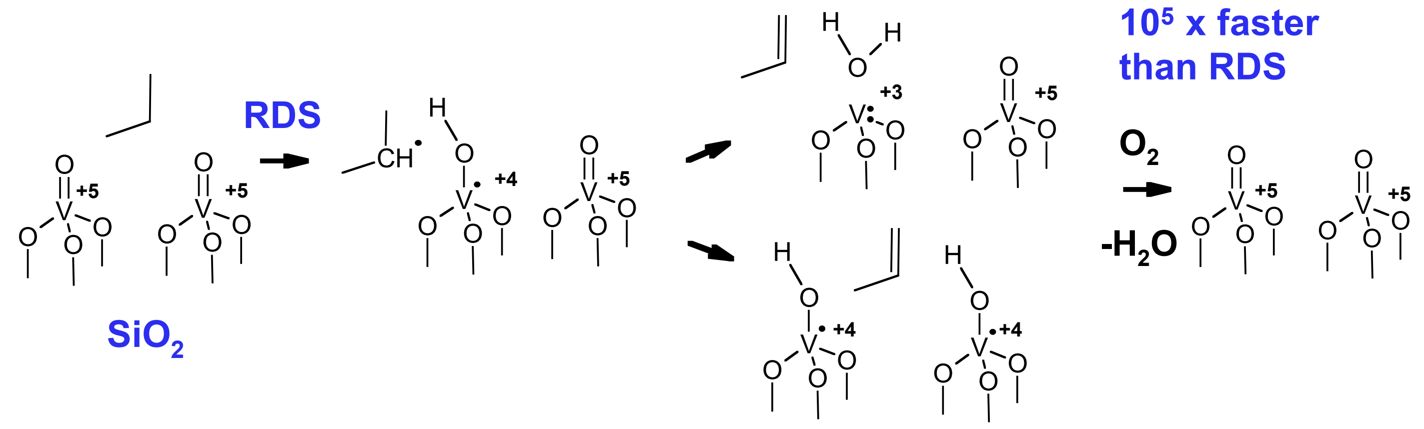
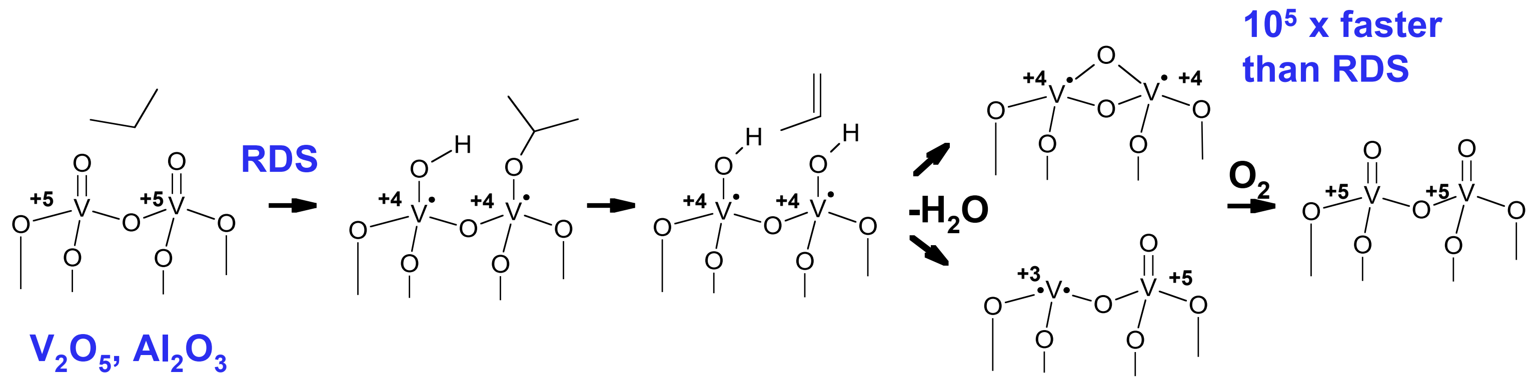
State of Research – Mechanisms ODP

(1)



Rozanska, X.; Fortrie, R.; Sauer, J. J. Phys. Chem. C ***2007****, 111, 6041-6050.*

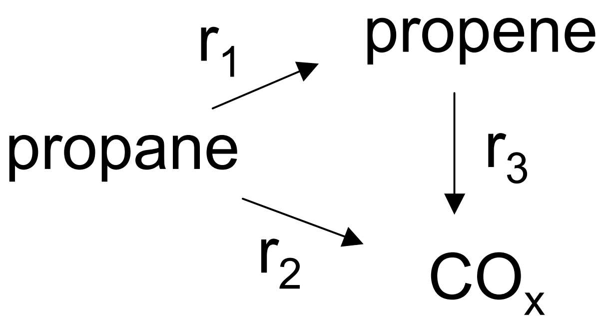
(2)



Gilardoni, F.; Bell, A. T.; Chakraborty, A.; Boulet, P. J. Phys. Chem. B ***2000****, 104, 12250-12255.*

Chen, K. D.; Khodakov, A.; Yang, J.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, *186*, 325-333.

Description of the reaction network:



$$C_3H_8 + [V^{+V}O] \rightarrow C_3H_6 + H_2O + [V^{+III}]$$

$$C_3H_8 + 7\,[V^{+V}O] \rightarrow 3\,CO + 4\,H_2O + 7\,[V^{+III}]$$

$$C_3H_8 + 10\,[V^{+V}O] \rightarrow 3\,CO_2 + 4\,H_2O + 10\,[V^{+III}]$$

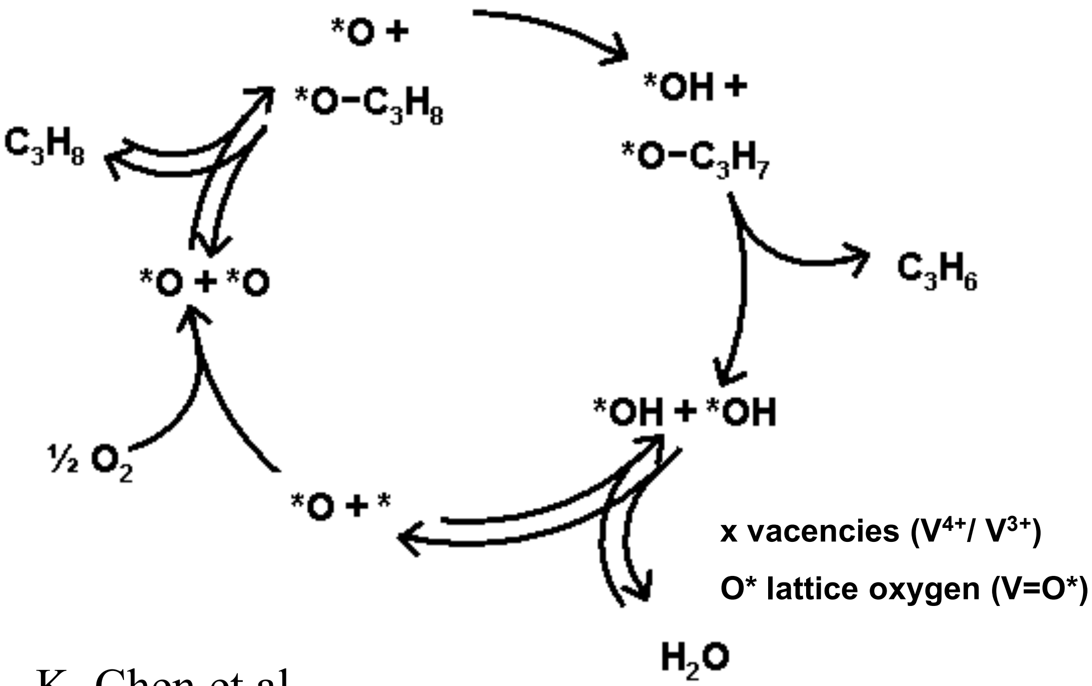
$$C_3H_6 + 6\,[V^{+V}O] \rightarrow 3\,CO + 3\,H_2O + 6\,[V^{+III}]$$

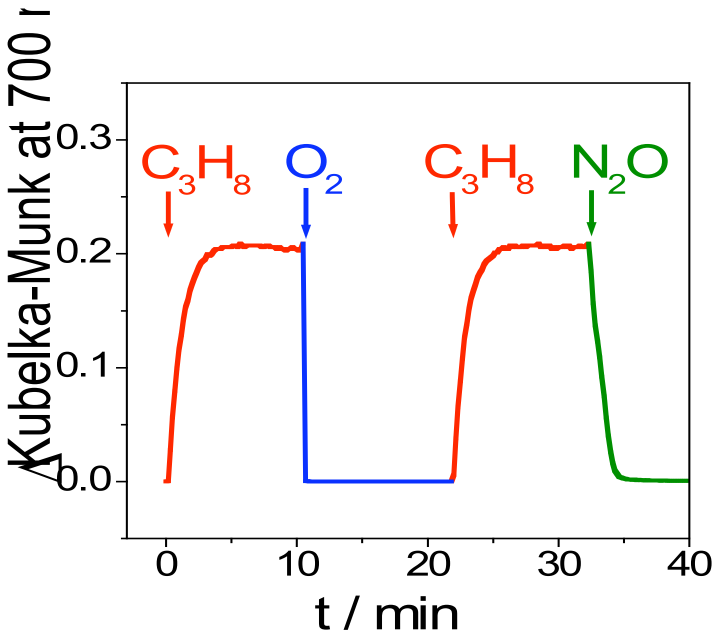
$$C_3H_6 + 9\,[V^{+V}O] \rightarrow 3\,CO_2 + 3\,H_2O + 9\,[V^{+III}]$$

$$CO + [V^{+V}O] \rightarrow CO_2 + [V^{+III}]$$

$$0.5\,O_2 + [V^{+III}] \rightarrow [V^{+V}O]$$

The catalytic cycle of ODP:





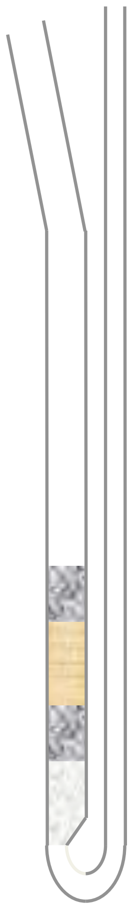
K. Chen et al.,
J. Catal. 192 (2000) 197

$$r_{MvK} = \frac{k_{red}\ K_{C_3H_8}\ p_{C_3H_8}}{\left\{1 + \left(K_{H_2O}\ p_{H_2O}\right)^{0.5} \times \left(\frac{k_{red}\ K_{C_3H_8}\ p_{C_3H_8}}{2\ k_{ox}\ p_{O_2}}\right)^{0.25}\right\}^2}$$

$$r_1 = k_1\ K_1\ c_{propane}$$

$$r_3 = k_3\ K_3\ c_{propene}$$

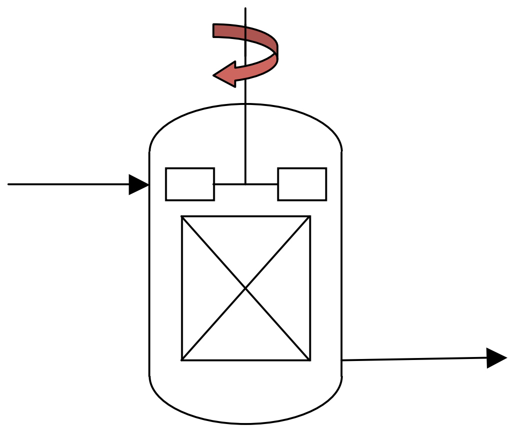
Measurements of ODP rates:



Tubular reactor

$$X = \frac{c_0 - c}{c_0} = 1 - \frac{c}{c_0}$$

$$r = \frac{dc}{dt} = c_0 \frac{dX}{dt} \approx c_0 \frac{\Delta X}{\Delta t}$$



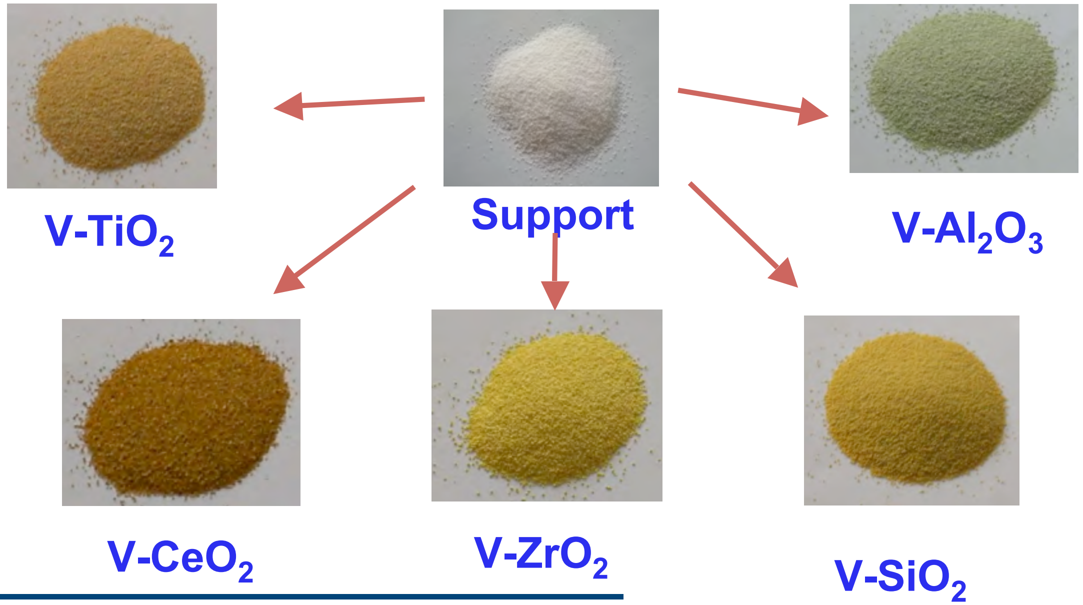
Gradientless Reactor

$$r_1 = k_1 K_1 c_{propane} = k_{eff} c_{propane}$$

$$\frac{\partial \ln k_{eff}}{\partial \, {}^1\!/_T} = -\frac{E_A + \Delta H_{add}}{R}$$

$$TOF = \frac{r}{c_{VO_x}}$$

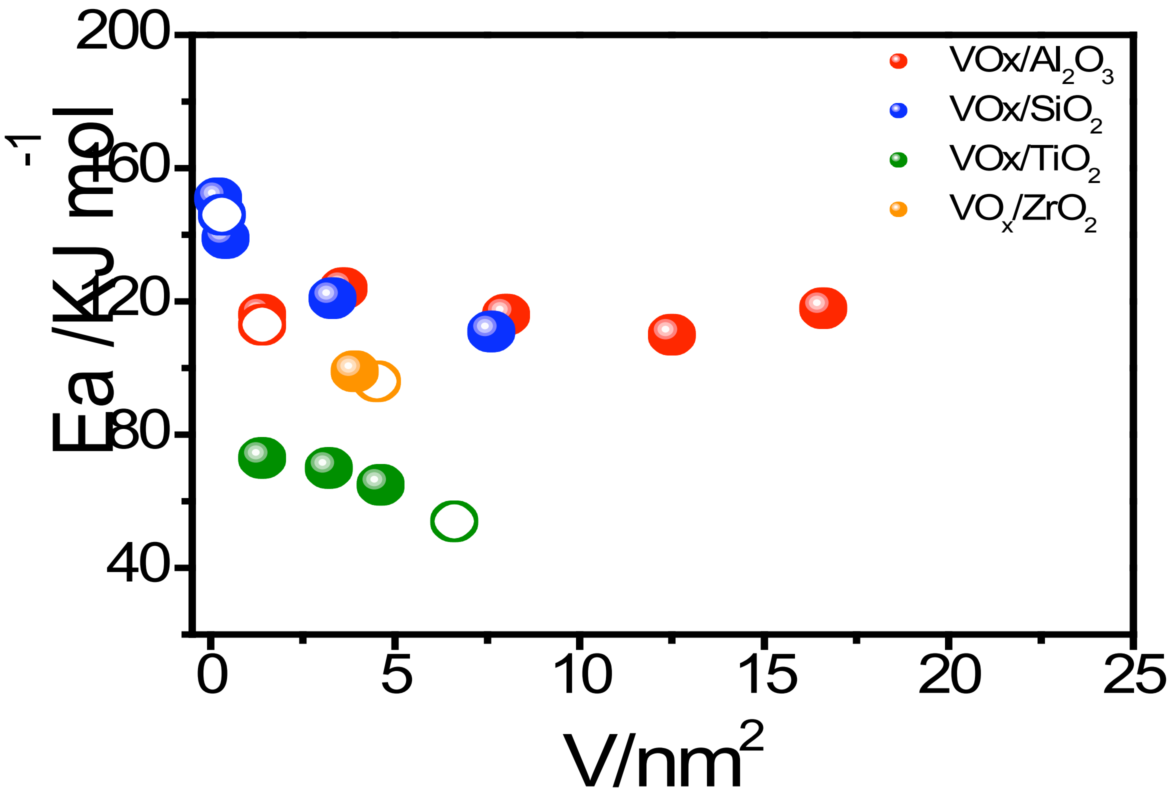
Catalyst with different support materials



	surface area		loading	
catalyst	$m?g^{-1}_{cat}$	$m?g^{-1}_{support}$	$V\ nm^{-2}$	wt% V_2O_5
V-TiO_2	66	68	1.5	1.6
V-Al_2O_3	96	100	1.4	2.1
V-ZrO_2	108	110	1.0	1.6
V-SiO_2	151	154	0.3	0.6
V-CeO_2	60	62	1.5	1.4

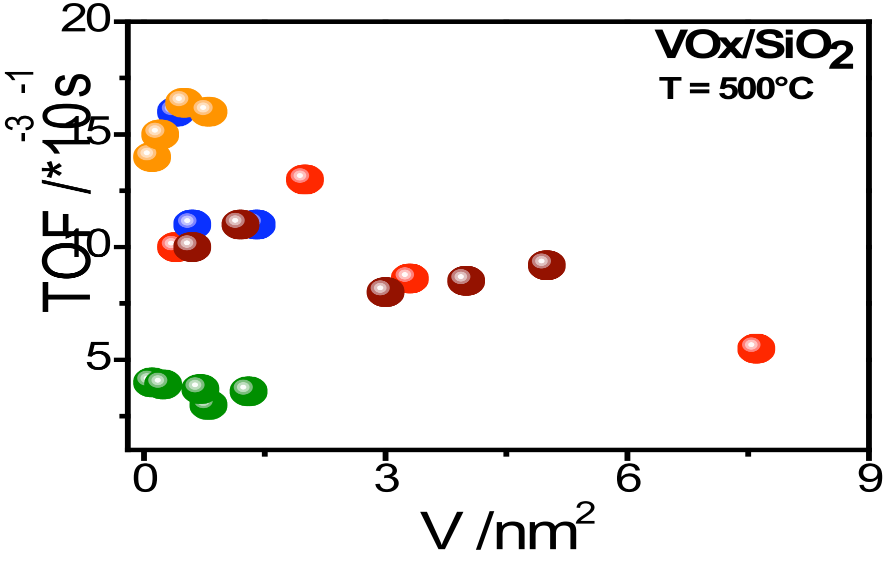
Catalysts prepared by saturation wetness impregnation.

A. Dinse, B. Frank, C. Hess, D. Habel and R. Schomäcker *J. Mol. Catal A: Chemical*, 28 - 37. 2008



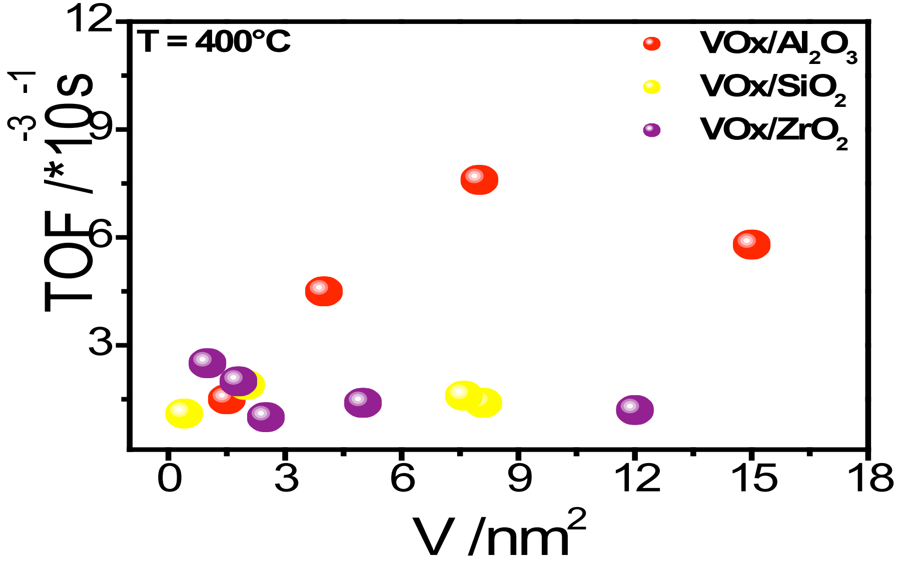
Oxidative dehydrogenation of propane activation energy, as a funtion of vanadia surface density on different VOx/support catalysts.

- Shee/Deo, Catalysis Today 118 (2006) 288
- Routry/Deo, Applied Catalysis A 265 (2004) 103
- Carrero/Schomäcker “in preparation”
- Pieck/Fierro, Journal of Catalysis 224 (2004) 1
- Argyle/Iglesia, Journal of Catalysis 208 (2002) 139
- Chen/Iglesia, Journal of Physical Chemestry 104 (2000) 1292
- Dinse/Schomäcker Journal of Molecular Catalysis A: Chemical 289 (2008) 28



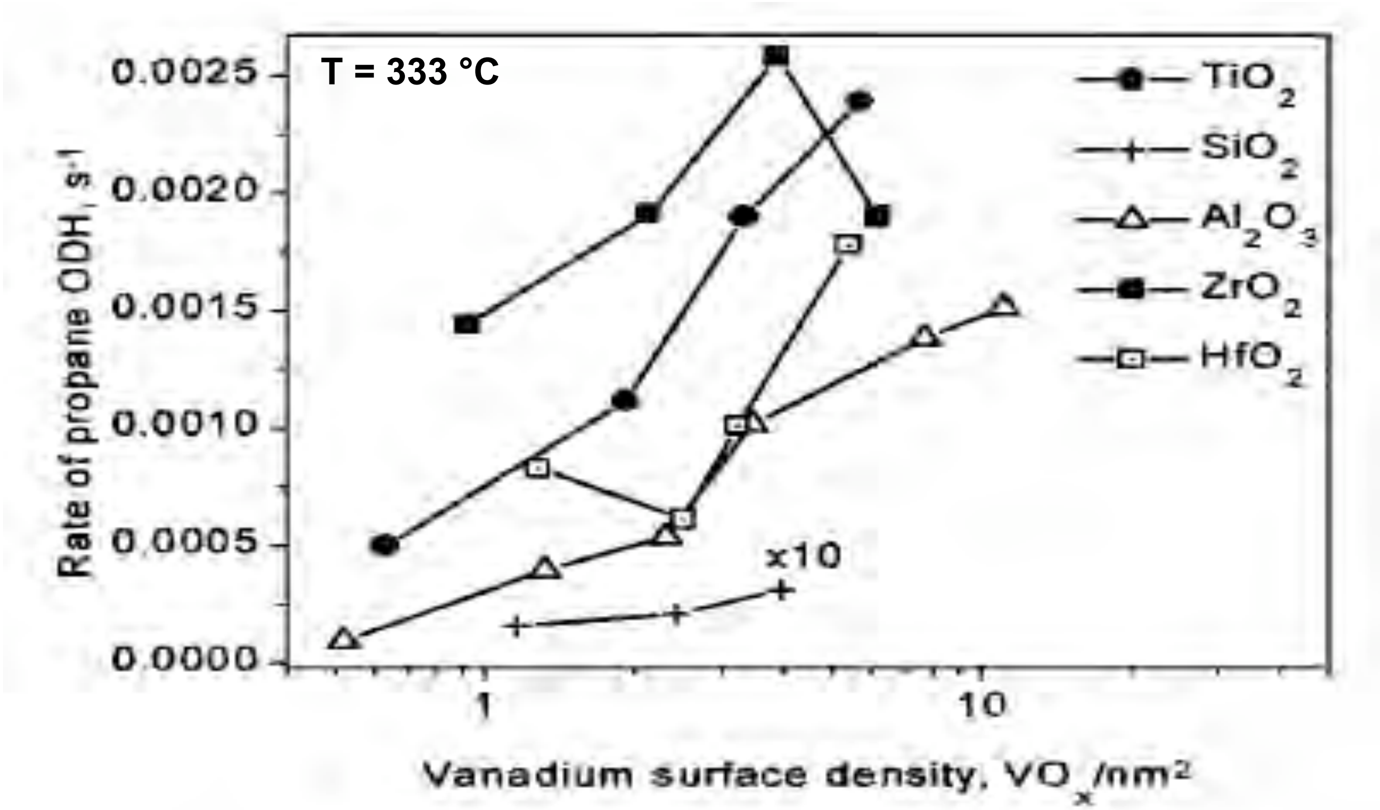
TOF of propane as a function of VO_x surface density at 500°C using different VO_x/SiO_2 catalysts. (SiO_2,MCM41,MCM48,SBA15)

- Kondratenko/Baerns, Catalysis Today 112 (2006) 60
- Ovsitser,/Kondratenko J Phys Chem C 111 (2007) 8504
- Carrero/Schomäcker, “in preparation”
- Karakoulia/Lemonidou, Catalysis Today 141 (2009) 245
- Kondratenko/Wachs, Journal of Catalysis 234 (2005) 131



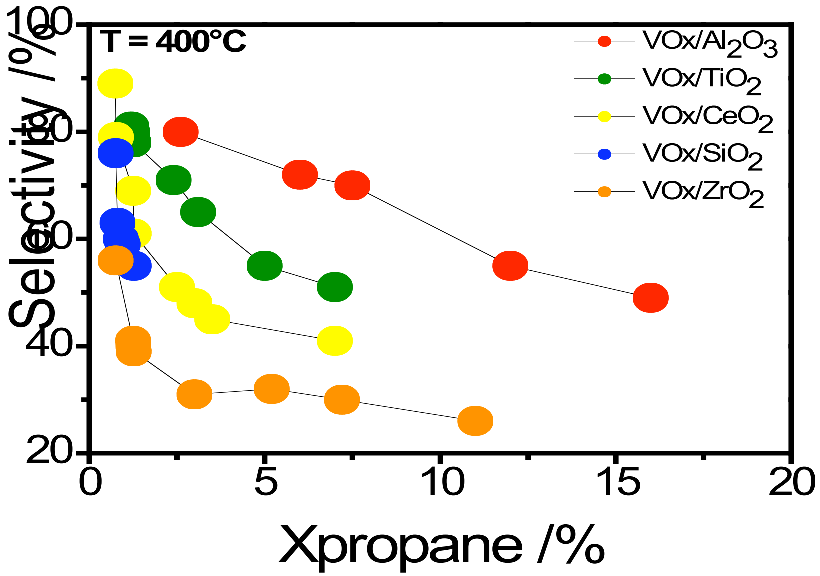
TOF of propane as a function of VO_x surface density at 400°C using different VO_x/support catalysts.

- Carrero/Schomäcker, “in preparation”
- Khodakov/Bell, Journal of Catalysis 177 (1998) 343
- Argyle/Iglesia, Journal of Catalysis 208 (2002) 139

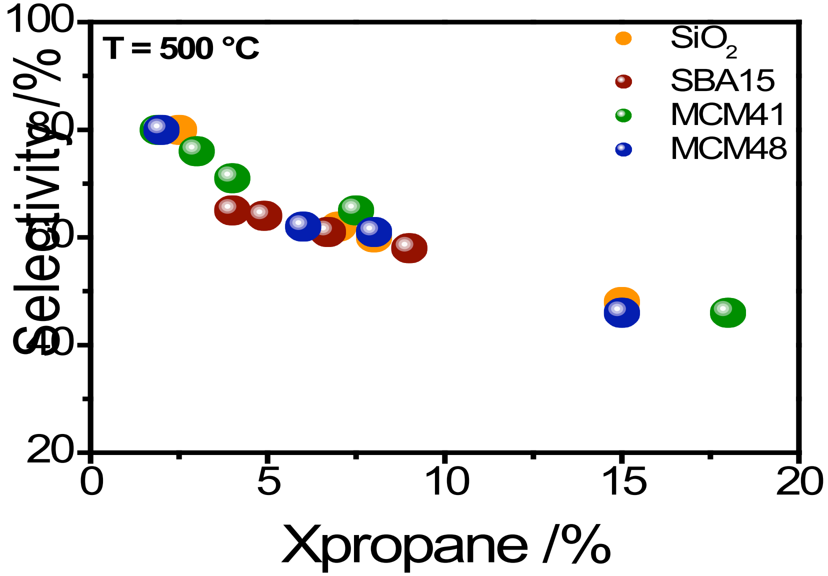


Effect of VO_x surface density on ODP rates (per V-atom)
. Reaction conditions: 333°C, 15.03kPa C_3H_8, 1.74 kPa O_2.

Khodakov/Bell, Journal of Catalysis 181 (1999) 205



Selectivity-conversion trajectories for different VO_x/support catalysts at 400°C.
$C_3H_8/O_2/N_2$ = 29.1/14.5/56.4 [*] .



Selectivity-conversion trajectories for different VO_x/support catalysts at 400°C.
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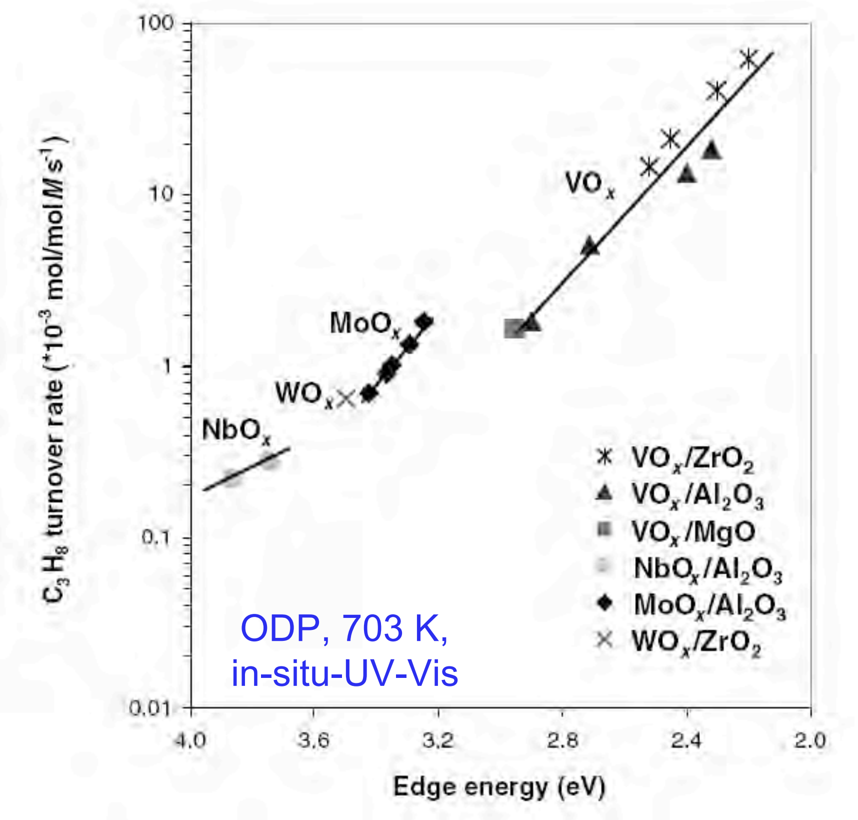
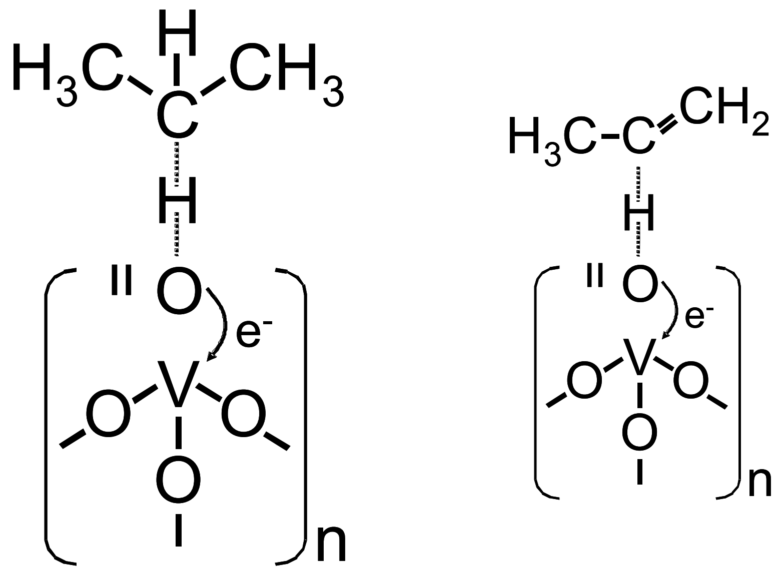
[*] Dinse/Schomäcker Journal of Molecular Catalysis A: Chemical 289 (2008) 28

Ovsitser,/Kondratenko J Phys Chem C 111 (2007) 8504

Carrero/Schomäcker “in preparation”





Reducebility (ability to delocalize electrons) as a measure for activity.

At equal loadings different cluster size responsible for change in activity/ reducebility?

Chen, K. D.; Bell, A. T.; Iglesia, E., J. Catal. ***2002****, 209, 35-42.*

Further kinetic parameter of the reaction network:

$$C_3H_8 + [V^{+V}O] \xrightarrow{k_1} C_3H_6 + H_2O + [V^{+III}] \qquad S_{propene}$$

$$C_3H_8 + 7\,[V^{+V}O] \rightarrow 3\,CO + 4\,H_2O + 7\,[V^{+III}]$$

$$C_3H_8 + 10\,[V^{+V}O] \rightarrow 3\,CO_2 + 4\,H_2O + 10\,[V^{+III}]$$

$$C_3H_6 + 6\,[V^{+V}O] \rightarrow 3\,CO + 3\,H_2O + 6\,[V^{+III}] \qquad S_{CO}$$

$$C_3H_6 + 9\,[V^{+V}O] \rightarrow 3\,CO_2 + 3\,H_2O + 9\,[V^{+III}] \qquad S_{CO2}$$

$$CO + [V^{+V}O] \rightarrow CO_2 + [V^{+III}]$$

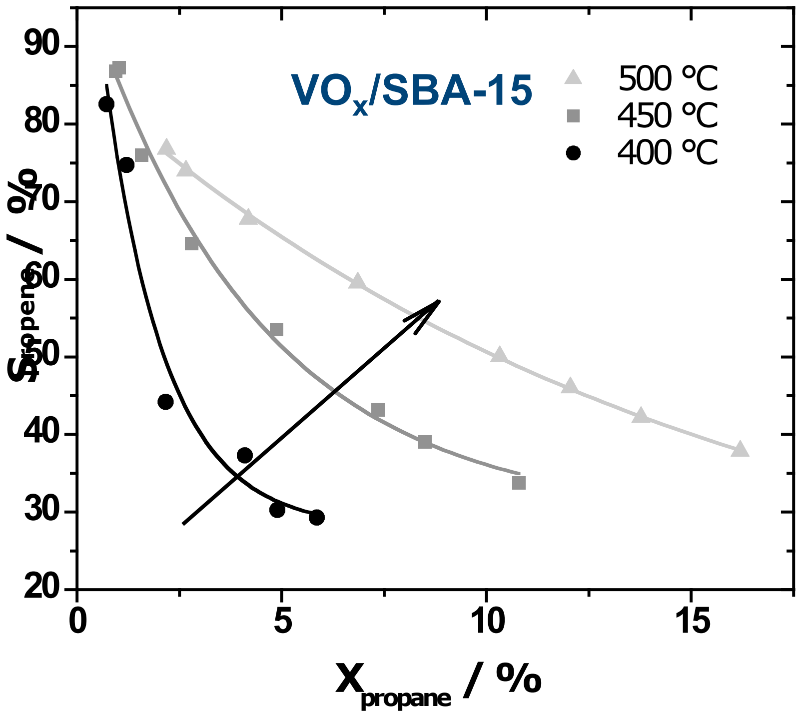
$$0.5\,O_2 + [V^{+III}] \rightarrow [V^{+V}O]$$

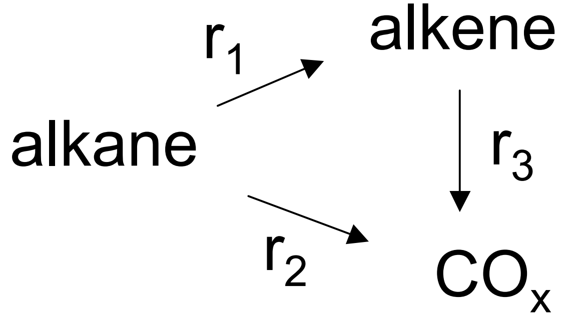
Table 2
Activation energies and TOF (400 °C) of ODP and propene combustion on differently supported vanadia catalysts

Catalyst	$E_{a,propane}$ (kJ mol^{-1})	$E_{a,propene}$ (kJ mol^{-1})	$TOF_{propane}$ (10^{-2} s^{-1})	$TOF_{propene}$ (10^{-2} s^{-1})
V-TiO_2	56 ± 5	147 ± 7	5.8 ± 0.2	47 ± 0.2
V-CeO_2	68 ± 6	101 ± 6	3.4 ± 0.2	14 ± 0.2
V-ZrO_2	78 ± 6	100 ± 6	5.6 ± 0.3	5.7 ± 0.3
V-Al_2O_3	113 ± 6	87 ± 5	0.68 ± 0.4	0.9 ± 0.2
V-SiO_2	146 ± 6	95 ± 5	0.13 ± 0.1	0.7 ± 0.1

$C_3H_x/O_2/N_2$ = 29.1/14.5/56.4 at a total gas flow of 60 ml min^{-1}.

Selectivity Data



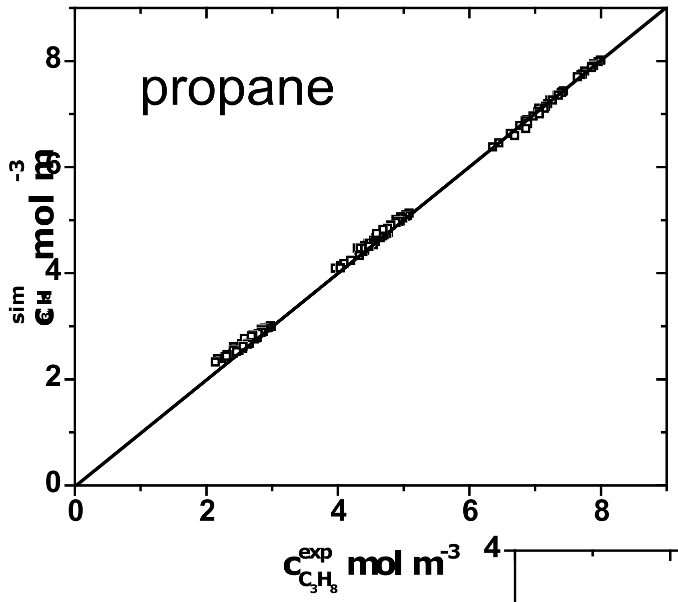


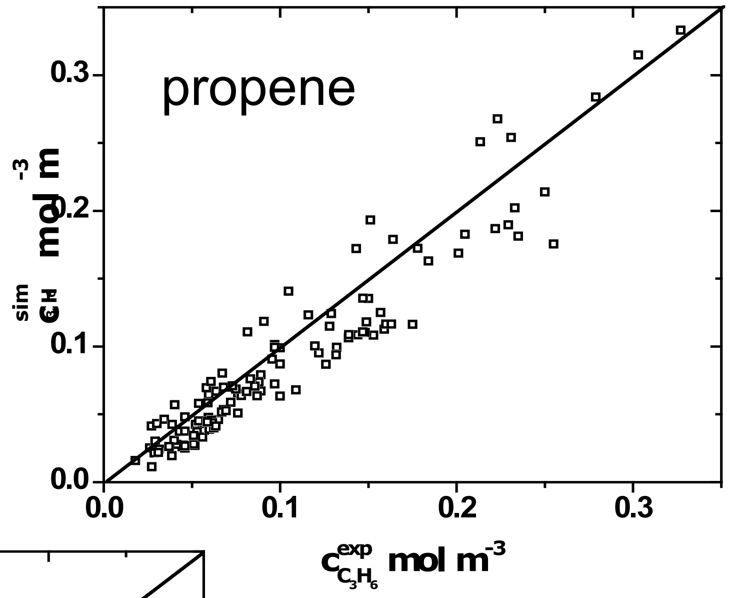
$$C_3H_8 \rightarrow C_3H_6 \rightarrow CO_x$$

$$E_{a,app}\,(C_3H_8) > E_{a,app}\,(C_3H_6)$$

$$X = 1 - \frac{c_{C_3H_8}}{c_{0,C_3H_8}} \qquad S = \frac{c_{C_3H_6}}{c_{0,C_3H_8} - c_{C_3H_8}}$$

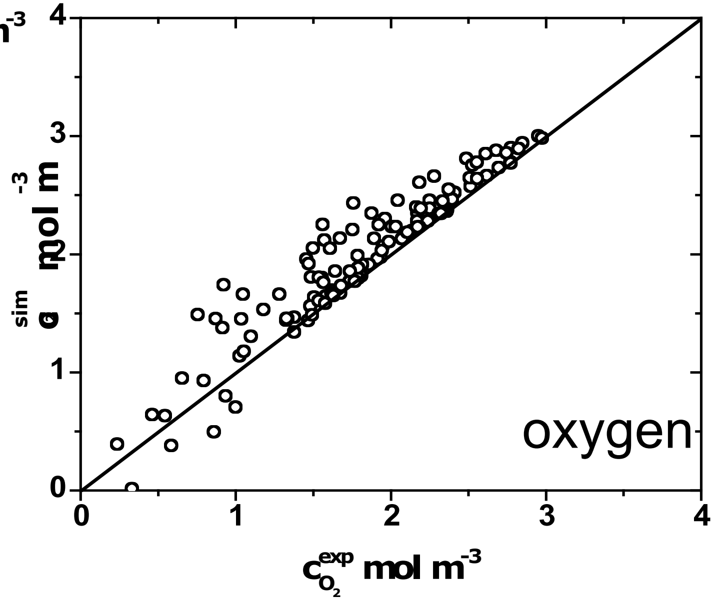
A. Dinse, S. Khennache, B. Frank, C. Hess. R. Herbert, S. Wrabetz, R. Schlögl, R. Schomäcker *Journal of Molecular Catalysis A: Chemical*, 307 (2009) 43





Propane/ O_2

1:1
2:1
4:1



Temperatures:
400, 425, 450,
475, 500 °C

Kinetics of ODP network

$$C_3H_8 \rightarrow C_3H_6 \rightarrow CO_x$$

$$r_1 = k_1 \cdot \exp\left(\frac{-E_{A1,app}}{R \cdot T}\right) \cdot c_{C_3H_8}^{m1} \cdot c_{O_2}^{m2}$$

$$r_2 = k_2 \cdot \exp\left(\frac{-E_{A2,app}}{R \cdot T}\right) \cdot c_{C_3H_6}^{m3} \cdot c_{O_2}^{m4}$$

	Propene formation			Propene combustion		
	$E_{A,1}$ kJ mol^{-1}	m_1	m_2	$E_{A,2}$ kJ mol^{-1}	m_3	m_4
VO_x/SBA-15	100±10	1	0	35±15	1	0

A. Dinse, S. Khennache, B. Frank, C. Hess. R. Herbert, S. Wrabetz, R. Schlögl, R. Schomäcker *Journal of Molecular Catalysis A: Chemical*, 307 (2009) 43

kinetics of reoxidation von V^{+III}

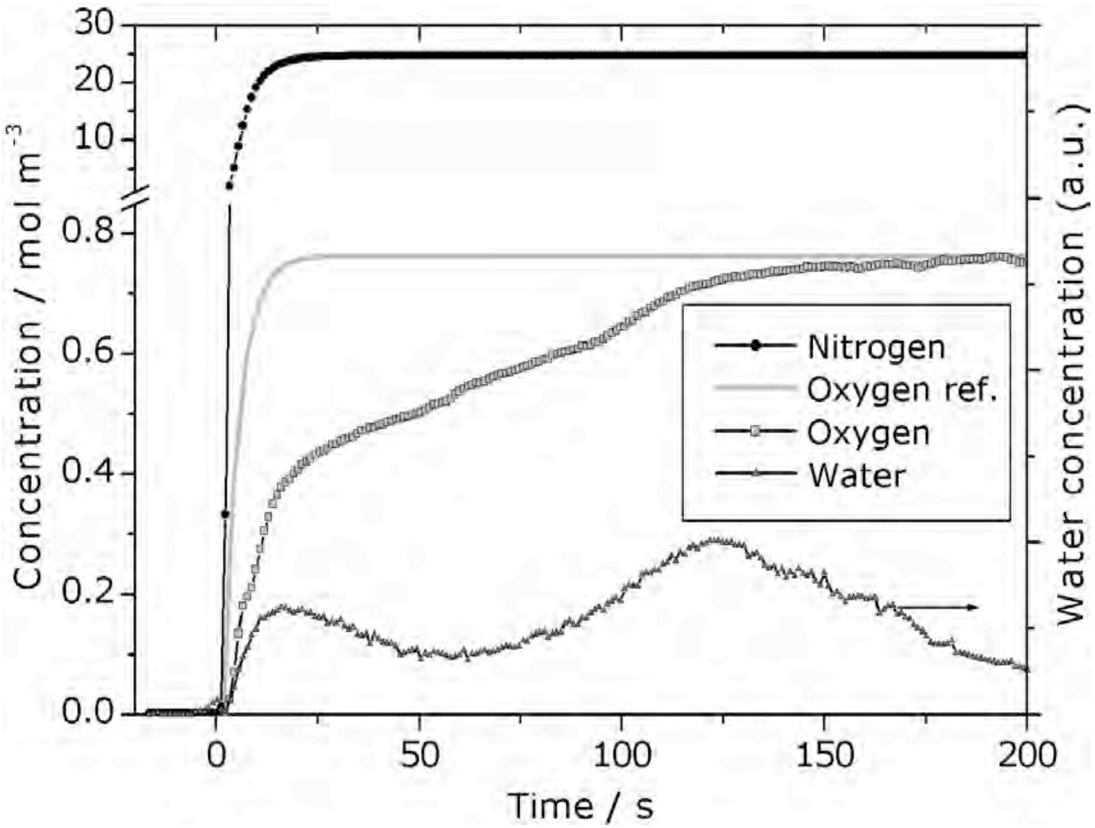
- Berty-Reaktor, step marking with O_2 with reduced catalyst ($V^{+III} + ½\, O_2 \rightarrow V^{+V}O$)
- Literature:

$$r = k\, c_{V^{+III}}^{m}\; c_{O_2}^{n}$$

Grabowski et al., *App. Catal. A* 242 (2003) 297
Routray et al., *Appl. Catal. A* 265 (2004) 103
Chen et al., *J. Catal.* 186 (1999) 325

1,0 g $VO_x/\gamma\text{-}Al_2O_3$,
d_p = 200 µm (VA-200),
479 K, 1 bar, 100 ml_n min^{-1}

3% O_2 in N_2



B. Frank, *Applied Catalysis A: General*, 288 - 295. 2009

kinetics of reoxidation von V^{+III}

Possible elementary steps:

(1) $H_2O + [V^{+III}] \rightarrow [V^{+III}OH_2]$

(2) $0.5\ O_2 + [V^{+III}OH_2] \rightarrow [V^{+V}(OH)_2]$

(3) $[V^{+V}(OH)_2] \rightarrow [V^{+V}O(OH_2)]$

(4) $[V^{+V}O(OH_2)] \rightarrow [V^{+V}O] + H_2O$

(5) $[V^{+III}OH_2] + [V^{+V}O] \rightarrow 2\ [V^{+IV}OH]$

(6) $0.5\ O_2 + [V^{+IV}OH] \rightarrow [V^{+V}O(OH)]$

(7) $[V^{+V}O(OH)] + [V^{+IV}OH] \rightarrow [V^{+V}O(OH_2)] + [V^{+V}O]$

B. Frank et al, *Applied Catalysis A: General*, 288 - 295. 2009

Resolution of reaction network

$$C_3H_8 + [V^{+V}O] \xrightarrow{k_1} C_3H_6 + H_2O + [V^{+III}]$$ $S_{propene}$

$$C_3H_8 + 7\,[V^{+V}O] \rightarrow 3\,CO + 4\,H_2O + 7\,[V^{+III}]$$

$$C_3H_8 + 10\,[V^{+V}O] \rightarrow 3\,CO_2 + 4\,H_2O + 10\,[V^{+III}]$$ S_{H2O}

$$C_3H_6 + 6\,[V^{+V}O] \rightarrow 3\,CO + 3\,H_2O + 6\,[V^{+III}]$$ S_{CO}

$$C_3H_6 + 9\,[V^{+V}O] \rightarrow 3\,CO_2 + 3\,H_2O + 9\,[V^{+III}]$$ S_{CO2}

$$CO + [V^{+V}O] \rightarrow CO_2 + [V^{+III}]$$

$$H_2O + [V^{+III}] \rightarrow [V^{+III}OH_2]$$

$$0.5\ O_2 + [V^{+III}OH_2] \rightarrow [V^{+V}(OH)_2]$$

$$[V^{+V}(OH)_2] \rightarrow [V^{+V}O(OH_2)]$$

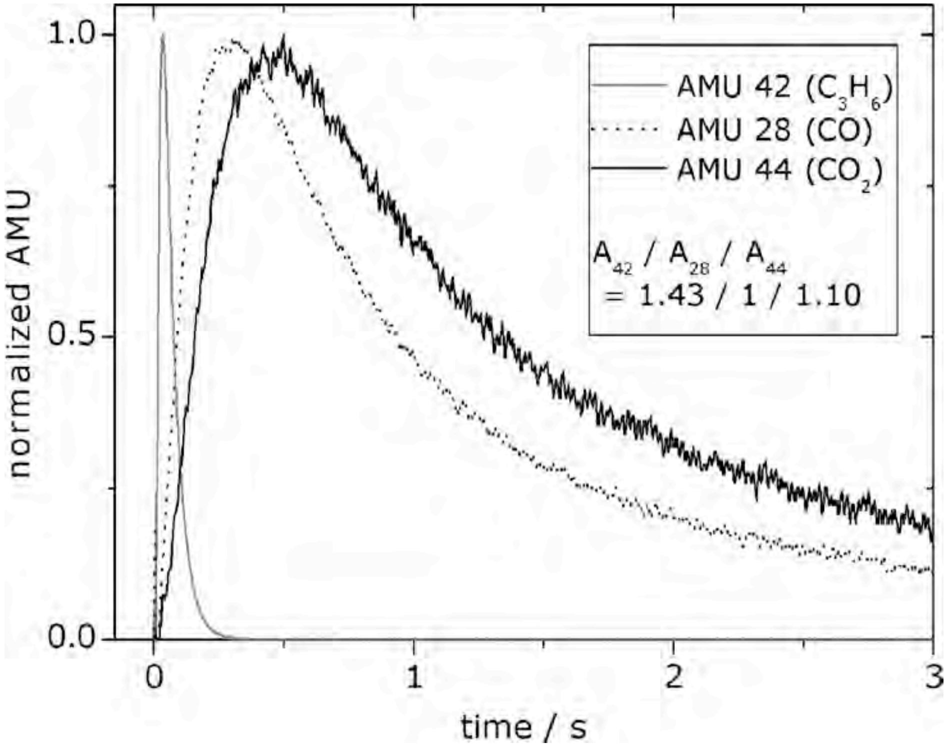
$$[V^{+V}O(OH_2)] \rightarrow [V^{+V}O] + H_2O$$

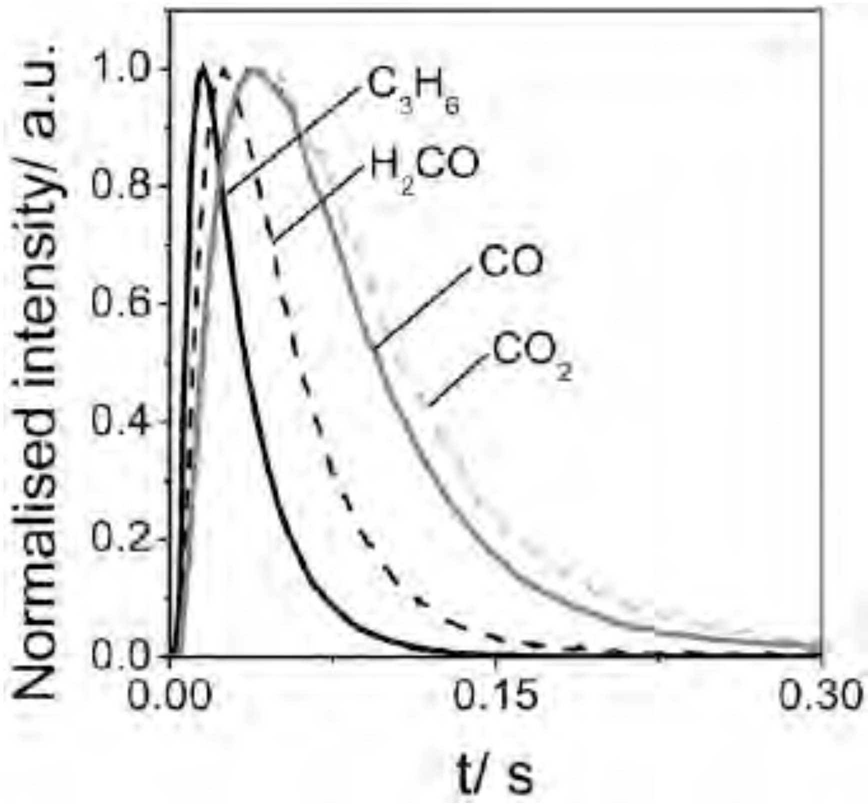
$$[V^{+III}OH_2] + [V^{+V}O] \rightarrow 2\ [V^{+IV}OH]$$

$$0.5\ O_2 + [V^{+IV}OH] \rightarrow [V^{+V}O(OH)]$$

$$[V^{+V}O(OH)] + [V^{+IV}OH] \rightarrow [V^{+V}O(OH_2)] + [V^{+V}O]$$

Transient experiments (TAP)





Propene pulsing over VA-200 sample VO_x/Al_2O_3 (1,4 Gew.-% V)

Propene pulsing over VO_x/Al_2O_3 (9,5 Gew.-% V)

E.V. Kondratenko, N. Steinfeldt, M. Baerns, *Phys. Chem. Chem. Phys.* **2006** *8* 1624

Conclusions

Intrinsic kinetic data available for

- structure-reactivity-correlations
- comparison with theoretical predictions
- microkinetic modelling

But:

- too little information in selectivity data to resolve complete network of elementary reactions
- requires extensive transient experiments and *in situ* spectroscopy of the catalyst