SFB 546
HU Berlin

Catalysis

From a kinetic analysis to an advanced performance of highly dispersed VO_x-species in conversion of C_3-C_4 alkanes to olefins

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SFB 546 „*Übergangsmetalloxid-Aggregate*“ Teilprojekt B3 (Kondratenko/Schomäcker)

Publications and presentations 2009-2010

Articles

1) E.V. Kondratenko, H. Wang, V.A. Kondratenko, and J. Caro, “Selective oxidation of CH_4 and C_2H_6 over a mixed oxygen ion and electron conducting perovskite: a TAP and membrane reactors study“
J. Molec. Catal. A: Chemical, 297 (2009) 142-149.

2) O. Ovsitser, and E.V. Kondratenko, “Similarity and differences in the oxidative dehydrogenation of C_2-C_4 alkanes over nano-sized VO_x species using N_2O and O_2“
Catal. Today, 142 (2009) 138-142.

3) M. Fait, R. Abdallah, D. Linke, E.V. Kondratenko, and U. Rodemerck, „ A novel multi-channel reactor system combined with operando UV/vis spectroscopy: proof of principles”
Catal. Today, 142 (2009) 196-201.

4) O. Ovsitser, M. Cherian, A. Brückner, and E.V. Kondratenko, ”Dynamics of redox behavior of nano-sized VO_x species over Ti-Si-MCM-41 from time-resolved in-situ UV/Vis analysis”,
J. Catal., 265 (2009) 8-18.

5) A. Simon, and E. V. Kondratenko, The Flash Method: A Shortcut For Producing The $Cs_x(W,Nb)_5O_{14}$ Structure”,
Chemistry: A European Journal 16 (2010) 1765-1767.

Publications and presentations 2009-2010

Talks

1) E.V. Kondratenko
“Using time-resolved methods to monitor and understand catalytic oxidation reactions “
plenary lecture at 6th World Congress on Oxidation Catalysis, Lille, France, 05-10.07.2009.

2) E.V. Kondratenko
”Mechanistic insights into the role of oxidant in catalytic conversions of small molecules”
Festkolloquium anlässlich des 75. Geburtstages von Professor Manfred Baerns, 23.09.2009, Rostock, Deutschland

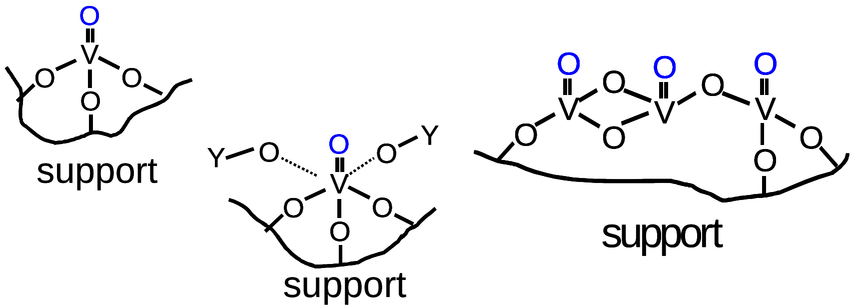
3) E.V. Kondratenko
”Catalytic removal of nitrogen oxides. A mechanistic view from transient experiments”
Seminar at the Institute of Technical Chemistry, University of Leipzig, Germany, 05.05.2009.

Background and materials

Selectivity and activity of VO_x aggregates in ODH strongly depends on:

- their structure
- surface density
- **reaction conditions**

VO_x(2-11 wt.%)/MCM-41(Ti/Si=0-1.5), VO_x(1-5 wt.%)/SiO_2



Can we force VO_x species to work selective at high degrees of alkane conversion ?

V surface density ~ 0.4 - 0.7 V/nm^2
(< 5-10% of V monolayer)

Experimental: Catalytic tests

Oxidative dehydrogenation of C_2-C_4 alkanes

Broad range of operation conditions:

P_{total} = 1 bar, T= 673-873 K

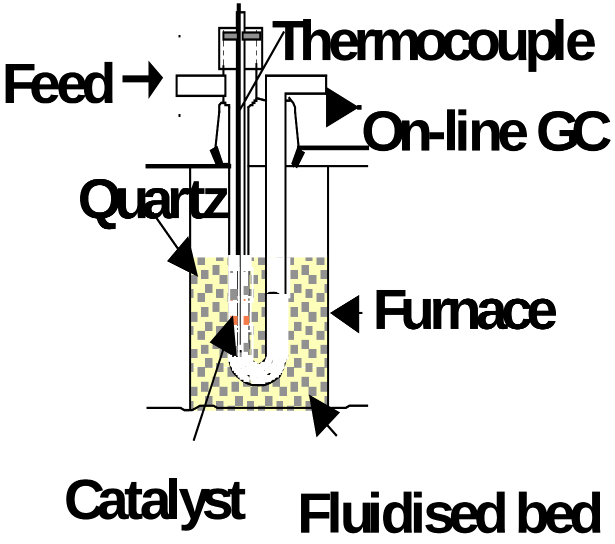
C_nH_{2n+2}: O_2: Ne = (5-100) : (0-20) : (1-40)

C_nH_{2n+2}:N_2O:Ne = (5-100) : (0-40) : (1-20)

Strong variation of oxidant content!

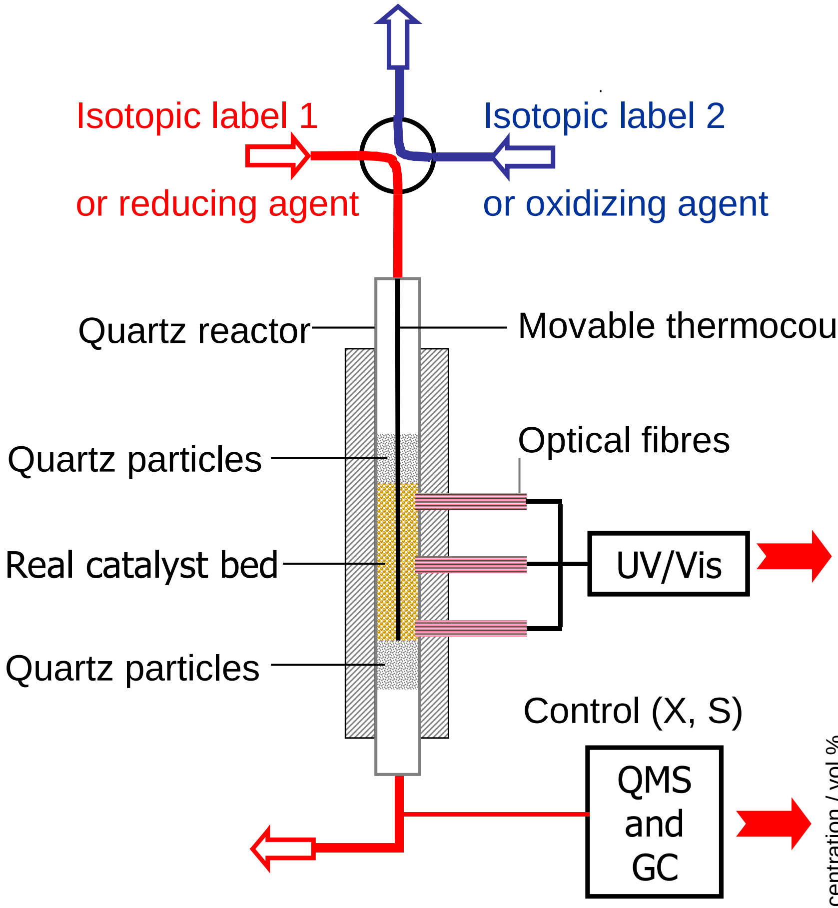
C_3H_8 + (O_2, N_2O) → C_3H_6

iso-C_4H_{10} + (O_2, N_2O) → iso-C_4H_8



Experimental: Characterization

in situ-UV/Vis



Isotopic label 1

or reducing agent

Isotopic label 2

or oxidizing agent

Quartz reactor

Movable thermocouple

Quartz particles

Optical fibres

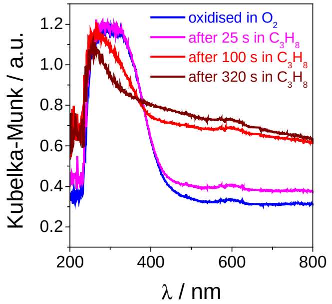
Real catalyst bed

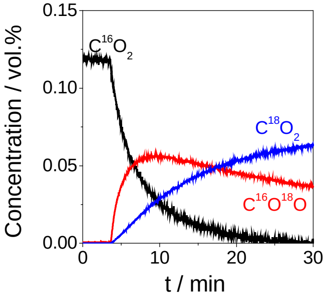
UV/Vis

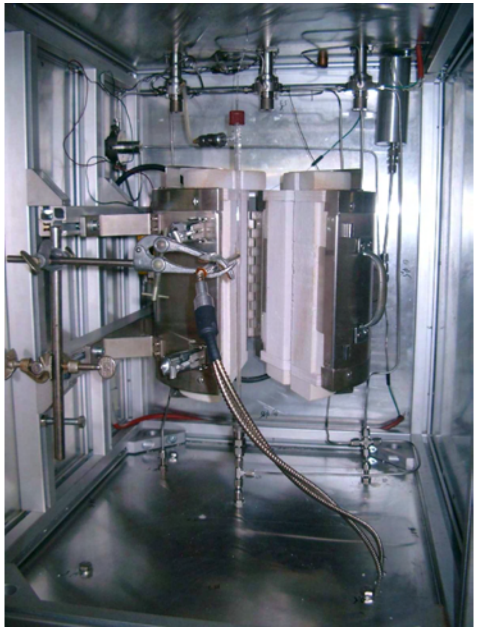
Quartz particles

Control (X, S)

QMS and GC





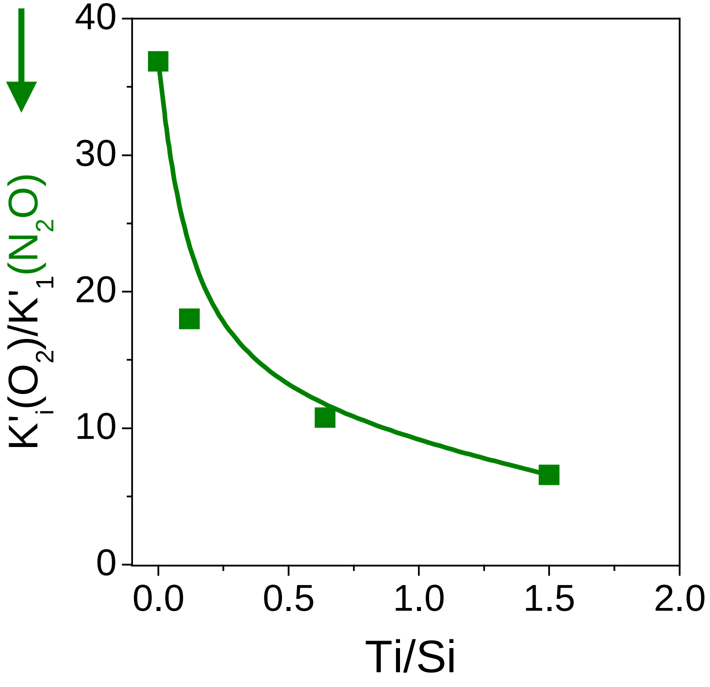


Technical data

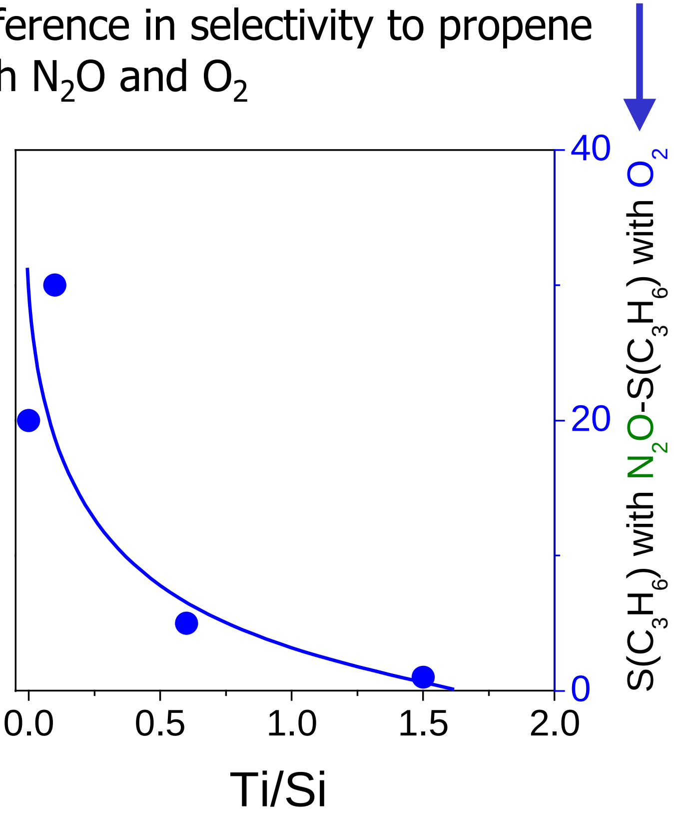
T up to 1073 K, **P** up to 15 bar, Fast UV/Vis analysis (every 1 s)
On-line MS analysis,
Fast valves for transient analysis

Correlation of catalyst selectivity and kinetic data

Difference in the reduction degree of VO_x species under ODP with O_2 and N_2O



Difference in selectivity to propene with N_2O and O_2

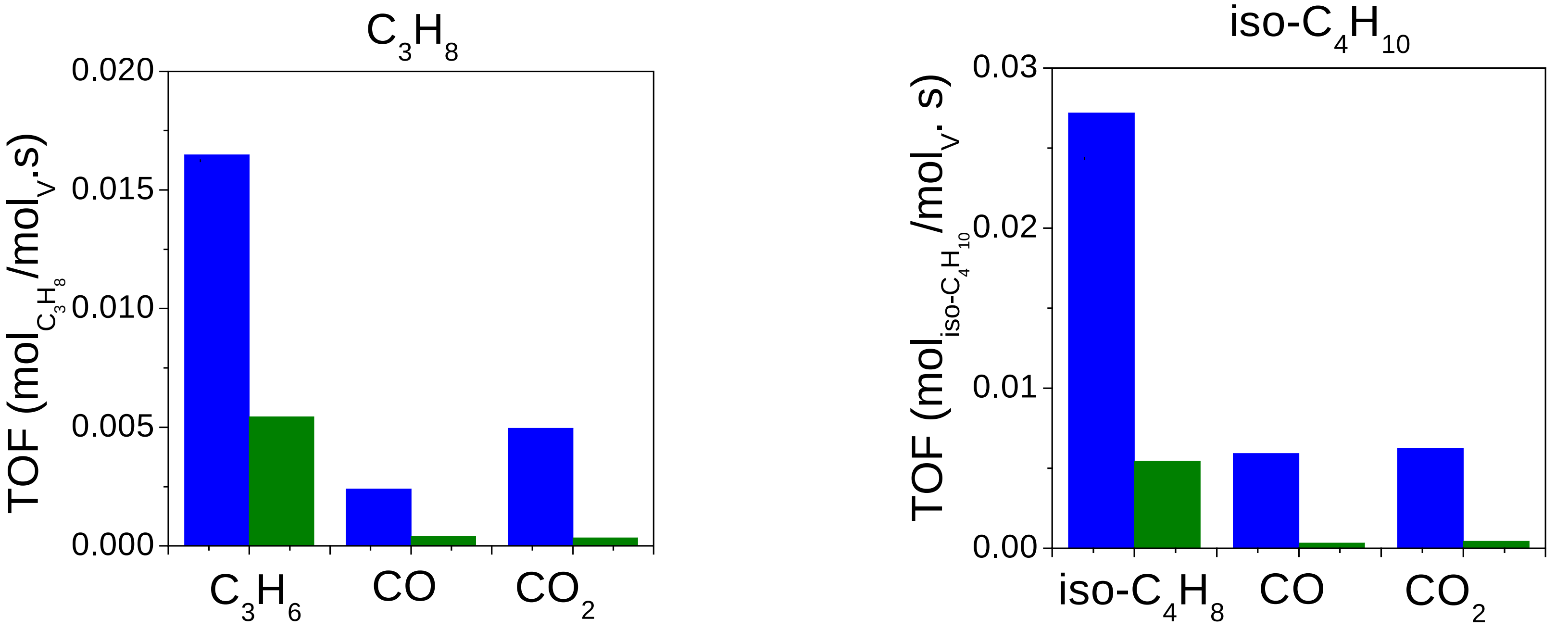


The reduction degree of VO_x species is an important selectivity-governing factor

O. Ovsitser et al., J. Catal., 265 (2009) 8.

Influence of O_2 and N_2O on catalytic performance of highly dispersed VO_x species in ODH reactions of C_3-C_4 alkanes

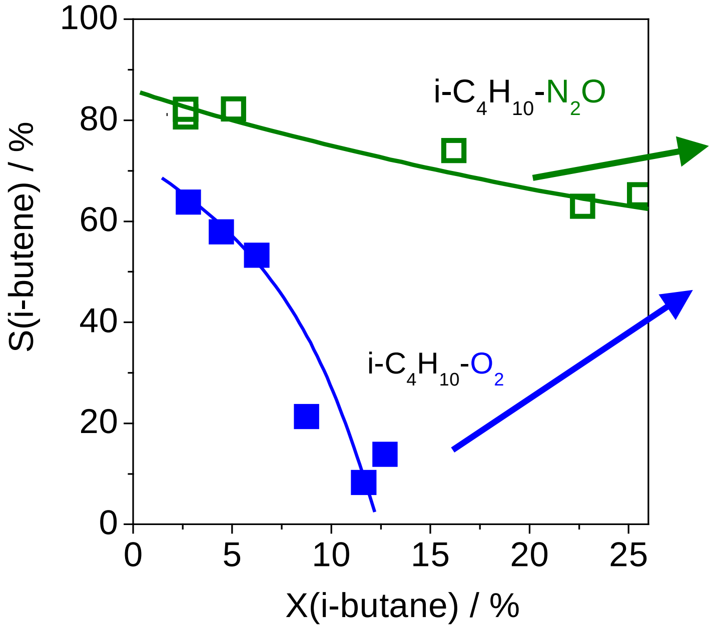
T = 773 K; same O-atoms content: C_nH_{2n+2}: O_2: Ne = 40 :20 :40; C_nH_{2n+2}:N_2O:Ne = 40 :40 :20



Nature of oxidant (O_2 , N_2O) strongly influences the activity and selectivity of VO_x species in ODH reactions

Influence of oxidant (concentration) on catalytic performance of highly dispersed VO_x species in ODH of iso-butane

Key aim is to improve olefin selectivity



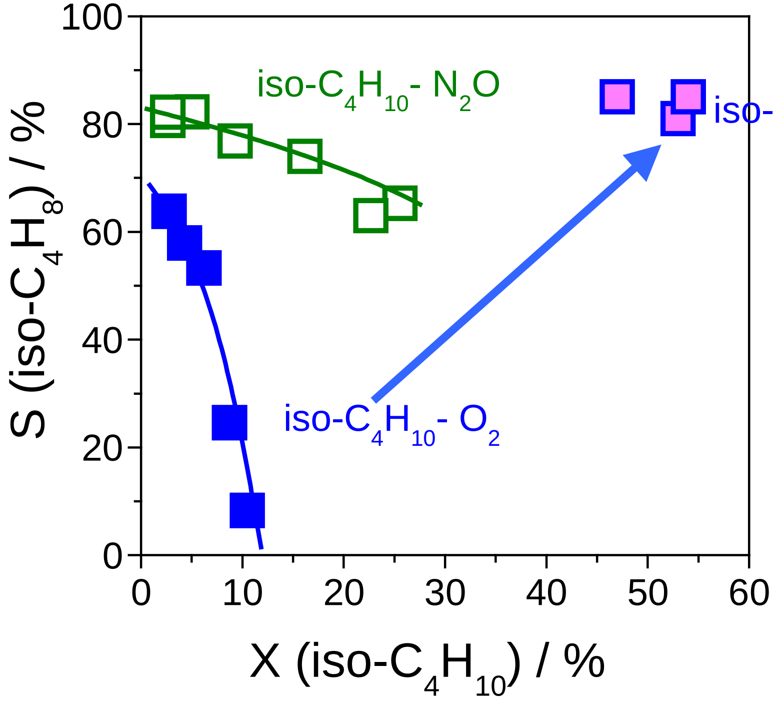
Industrially
interesting area

CO_x formation - decreases the olefin yield
- significantly dilutes outlet gasses

Can we minimized undesired CO_x formation further by variation of oxidant concentration? At high degree of alkane conversion…

Improving process selectivity of highly dispersed VO_x species in ODH of iso-butane

$VO_x(5)/MCM-41$, T = 773 - 833 K

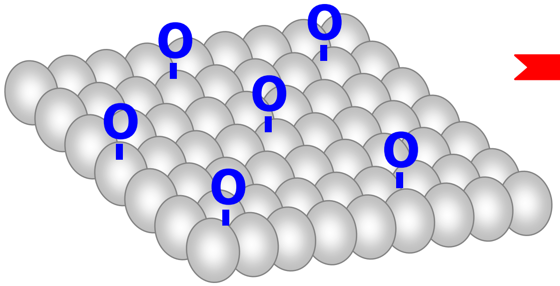


iso-C_4H_{10}- O_2 ← Oxygen lean conditions (iso-C_4H_{10}/O_2 >10)

Selectivity to iso-butene can be significantly improved by reducing of oxidant content!

K(reoxidation)/K(reduction) > 1, but $[O_2] << [C_4H_{10}]$

K(reoxidation)*$[O_2]$/K(reduction)* $[C_4H_{10}]$ < 1
High reduction degree



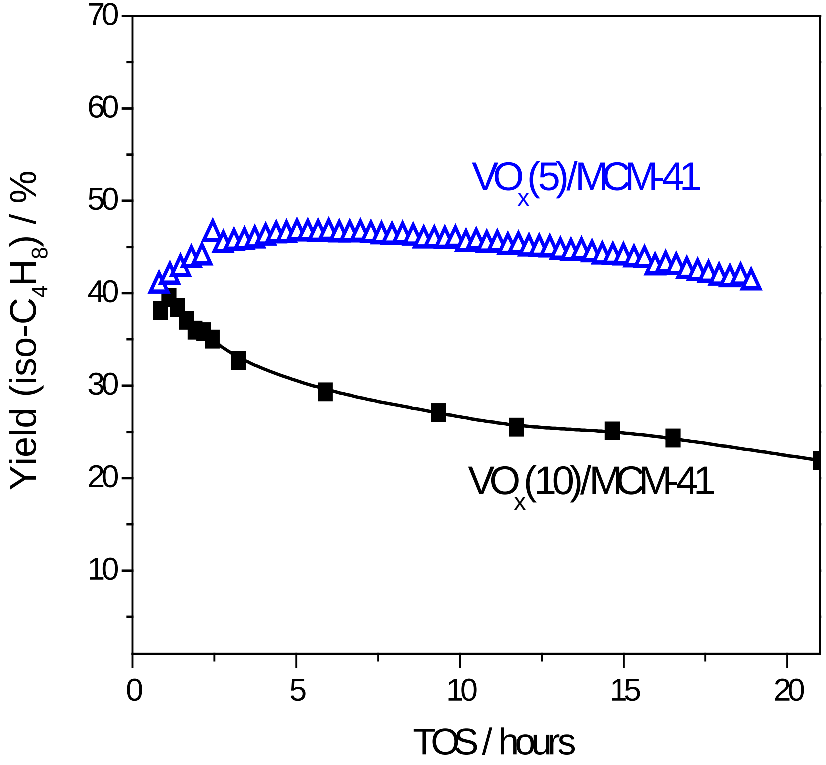
→ alkene (high)
CO_x (low)

O. Ovsitser, and E.V. Kondratenko, Catal. Today, 142 (2009) 138.

Improving process selectivity of highly dispersed VO_x species in ODH of iso-butane

T = 833 K; W/F=5 g s ml^{-1} for VO_x(5)/MCM-41 and W/F=15 g s ml^{-1} for VO_x(11)/MCM-41

iso-C_4H_{10}: - 15 %.



Amount of iso-C_4H_8 formed >O_2 passed in RM + O-in VO_x-species

Contribution of non-oxidative dehydrogenation?

- Yes. H_2 formation was confirmed by GC-analysis with Ar-carrier gas

Contribution of thermal dehydrogenation?

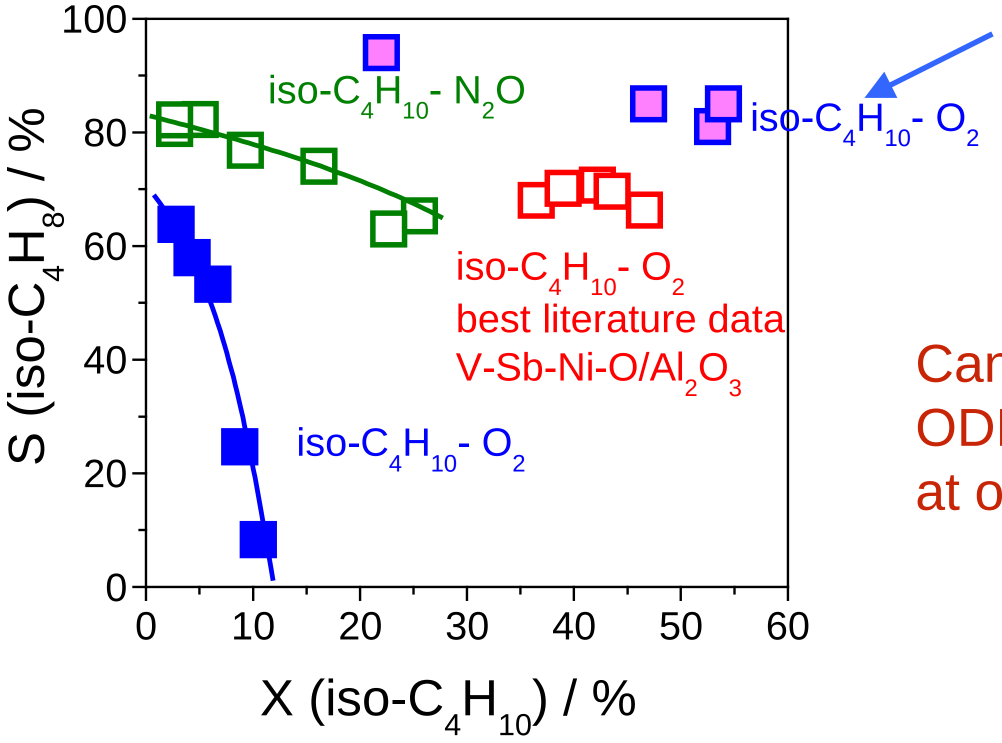
-No. At the same conditions $X_{iso\text{-}C_4H_{10}}$ < 0.3 % over quartz.

-Catalytic formation of olefins over VO_x-species.

Samples with highly dispersed VO_x-species (e.g. VO_x(5)/MCM-41) have shown best results

Improving process selectivity of highly dispersed VO_x species in ODH of iso-butane

Comparison of our results with literature data

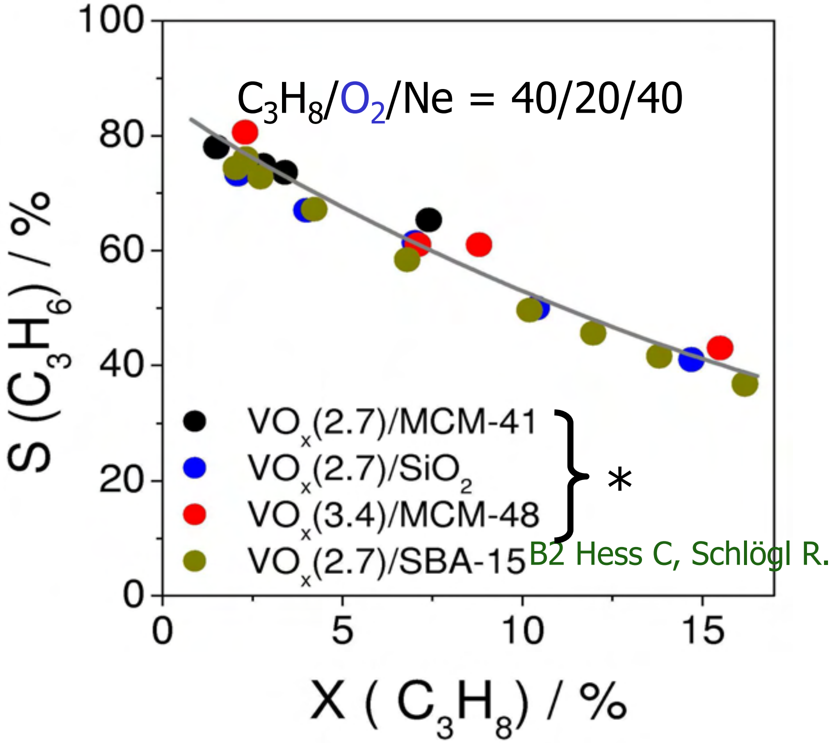


Oxygen lean conditions
(iso-C_4H_{10}/O_2 >10)

Can selectivity to propene in propane ODH be also improved by operation at oxygen-lean condition?

Improving process selectivity of highly dispersed VO_x species in ODH of propane

Comparison of our results with previous data

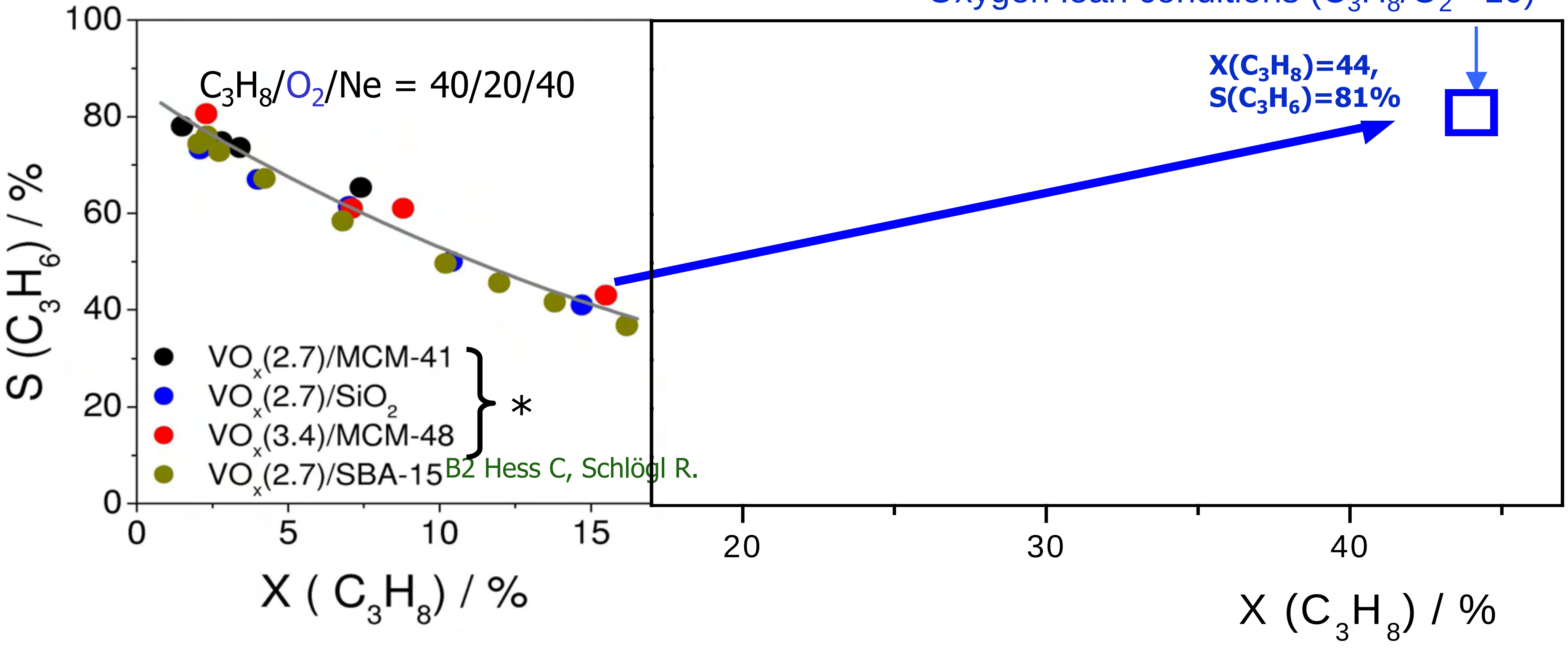


**Ovsitser O. et al., J. Phys. Chem. C, 111 (2007) 8595.*

Improving process selectivity of highly dispersed VO_x species in ODH of propane

Comparison of our results with previous data

Oxygen lean conditions (C_3H_8/O_2 >10)

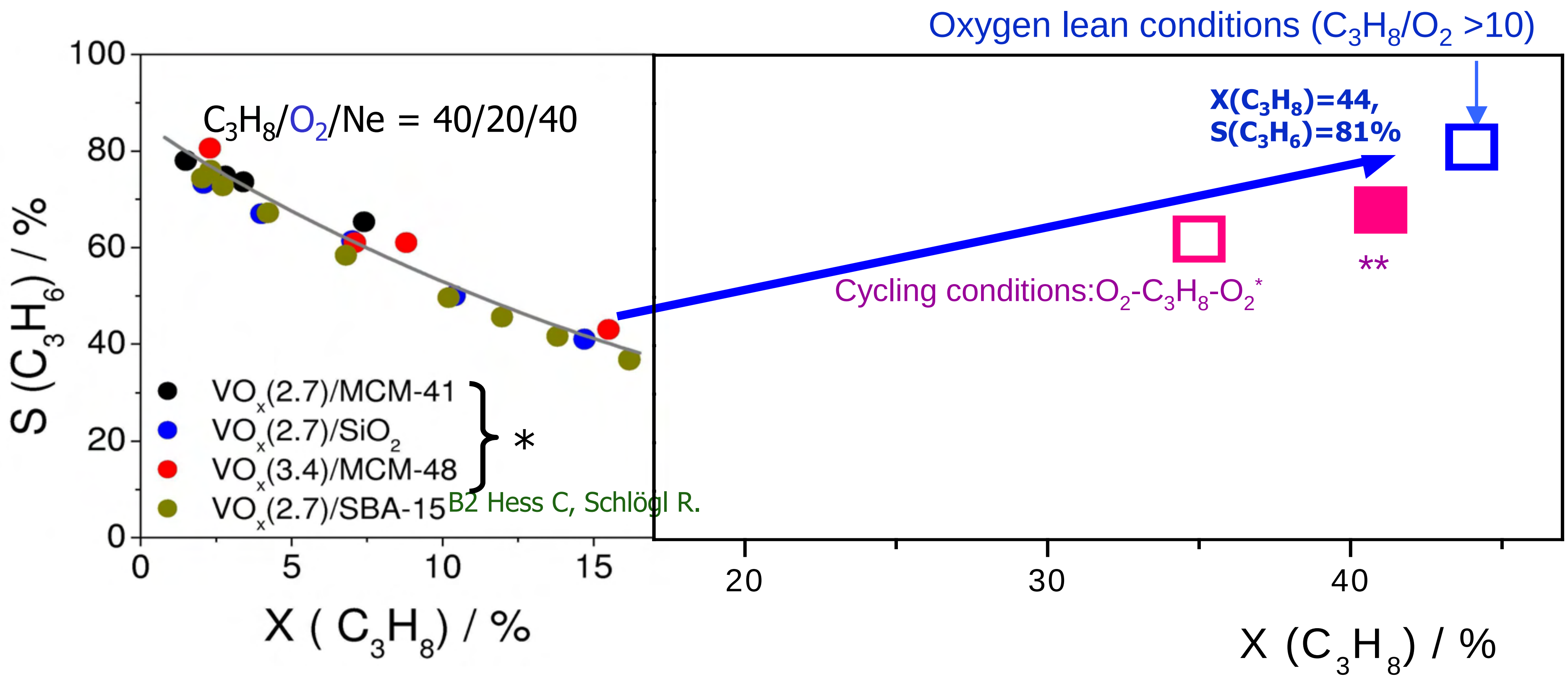


Ovsitser O. et al., J. Phys. Chem. C, 111 (2007) 8595.

Selectivity to propene can be significantly improved as well by reducing of oxidant content!

Improving process selectivity of highly dispersed VO_x species in ODH of propane

Comparison of our results with previous data and best literature data


Oxygen lean conditions (C_3H_8/O_2 >10)

$C_3H_8/O_2/Ne$ = 40/20/40

$X(C_3H_8)$=44,
$S(C_3H_6)$=81%

Cycling conditions: O_2-C_3H_8-O_2*

**

B2 Hess C, Schlögl R.

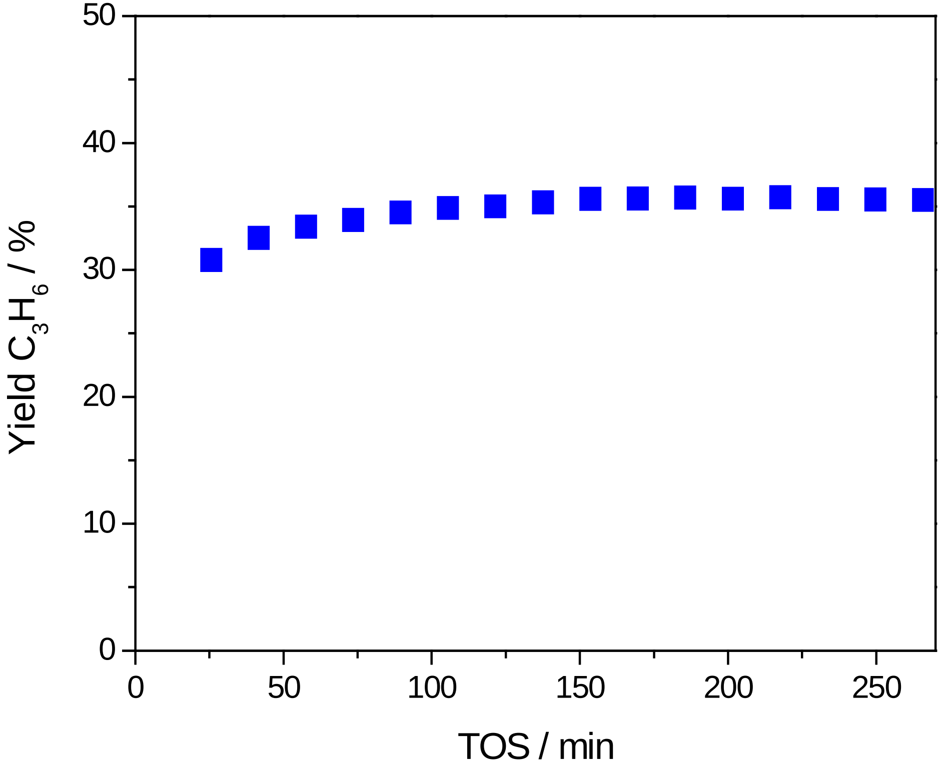
*Ovsitser O. et al., J. Phys. Chem. C, 111 (2007) 8595.

*Ballarini et al., J. Catal., 213 (2003) 95

**Liu Y.-M. et al., J.Catal. 224 (2004) 417

Selectivity to propene can be significantly improved as well by reducing of oxidant content!

Improving process selectivity of highly dispersed VO_x species in ODH of propane


VO_x(5)/MCM-41;T = 833 K, W/F=7 g s ml^{-1}

Stable catalytic performance was achieved over VO_x-species in propane dehydrogenation es well!

Formation of olefins over VO_x-species:

i) oxidative dehydrogenation during first minutes of operation under oxygen-free or oxygen-lean conditions,

ii) non-oxidative dehydrogenation of alkanes to olefins and hydrogen.

Their relative contribution to the overall olefin production depends on reaction condition (temperature, contact time) and oxygen content in reaction feeds.

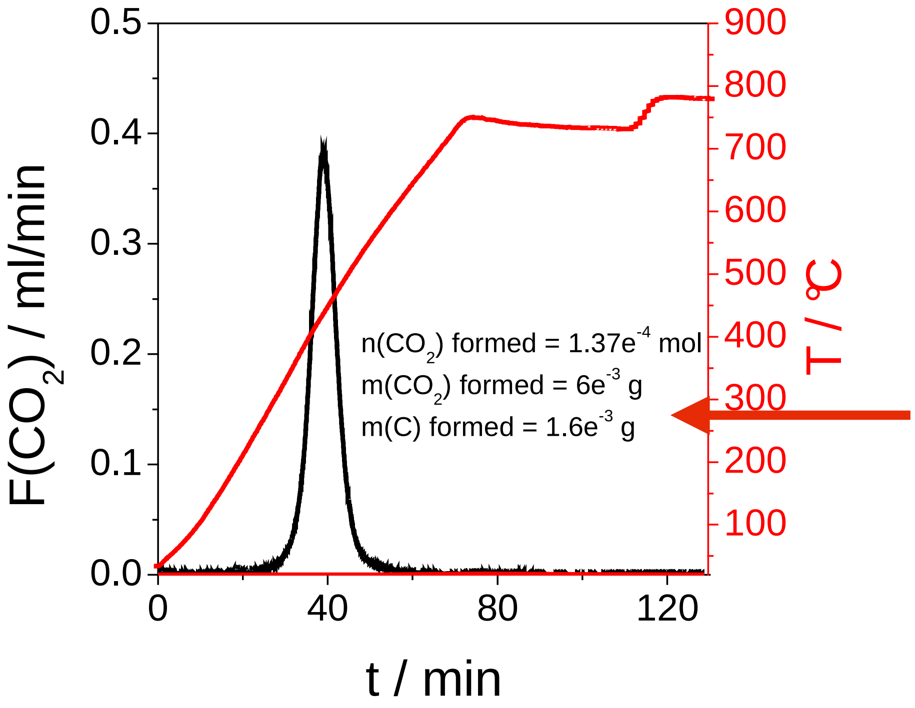
Recent papers confirm that considerable amounts of H_2 are produced under conditions of propane ODH, with vanadium oxide-based catalysts *, **

** Sinev M. Yu. et al., Catal. Today 81 (2003) 107*

*** Ballarini N. et al. Appl. Catal. A: 307 (2006) 148*

Improving process selectivity of highly dispersed VO_x species in ODH reactions of C_2-C_4 alkanes

TPO VO_x(1.3%)/SiO_2 (after 24 hours TOS in propane DH)



At optimal operation conditions formation of carbon deposition on the catalyst surface is very limited!!!

only ca. 0.3 wt.% to the catalyst mass after 24 hours of TOS in propane DH!

Such low coke formation is a reason of stable work of VO_x/Si-support catalysts, which do not possess strong acid-sites.

Conclusions

- Selective reaction pathways in ODH over VO_x-species can be controlled by variation of nature of oxidizing agent and their concentration, regulating oxygen species of certain reactivity, selectivity and concentration.

- Non-oxidative alkane dehydrogenation over VO_x-species offers an additional very selective pathway of olefins formation. Their relative contribution to the overall olefin production depends on reaction condition (temperature, contact time) and oxygen content in reaction feeds.

- VO_x-species can work very selectively in alkanes dehydrogenation reaction. Isobutene selectivity above 80% and CO_x selectivity below 2 % were achieved at isobutane conversions above 50%. In propane dehydrogenation, selectivity to propylene above 80% was achieved at propane conversion above 40%.This appears to be attractive for industrial applications.

- This knowledge in combination with deeper understanding of structural and surface properties of oxide catalysts may be useful for the development of catalytic materials or ways of operation, which can allow the production of olefins with high selectivity at alkane conversions as high as possible and minimized CO_x production.