B2/B6: VxOy (TixOy) in SBA 15:

SFB 546

Synthesis

Structure

ODH of propane

Who did the work

Reactivity group: A.Trunschke

G. Tzolova-Müller

J. Kröhnert

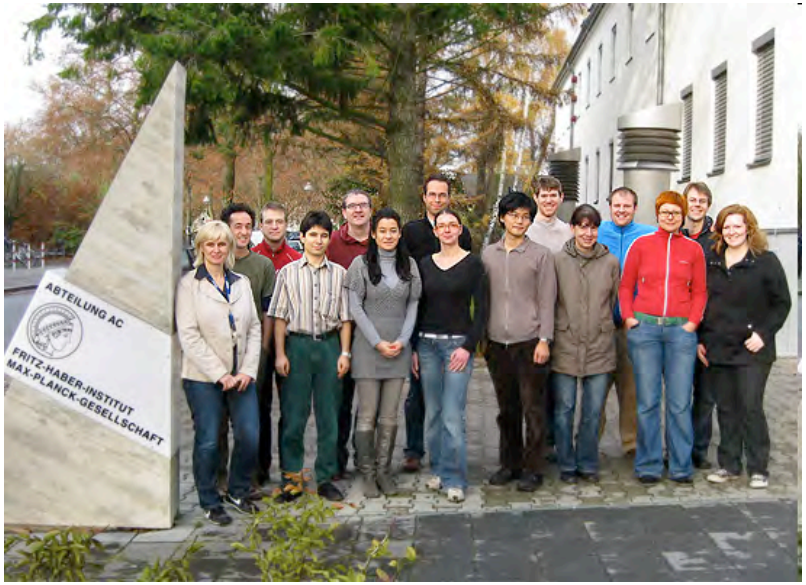
T. Wolfram

B. Frank

G. Weinberg & W. Zhang, A. Klein-Hoffmann
G. Lorenz & M. Hashagen & D. Brennecke
F. Girgsdies & E. Kitzelmann
M. Haevecker

R. Schlögl

- **FU:** K. Dinse
- **TU:** Schomäcker group : A. Dinse, C. Carrero

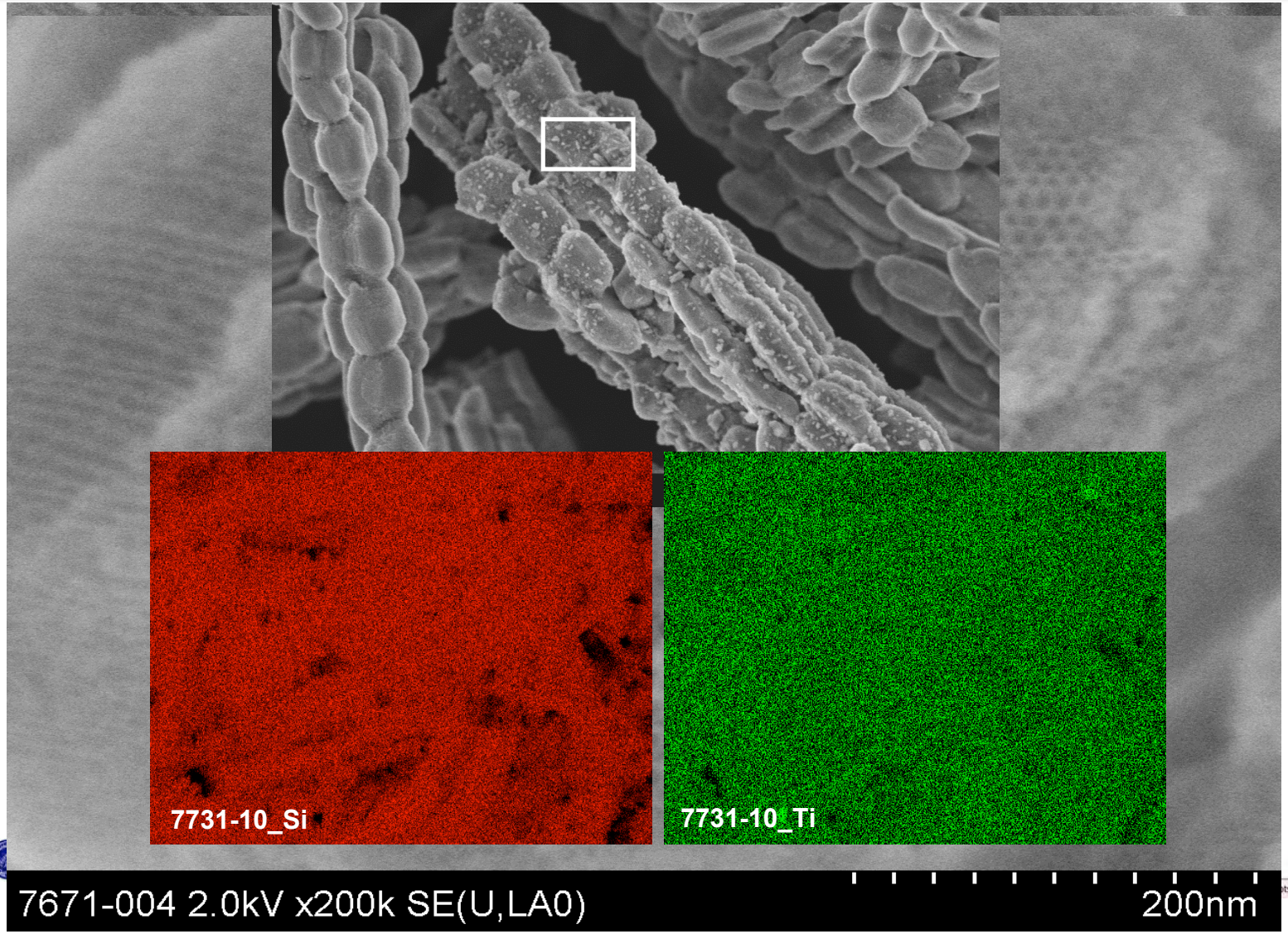


Targets

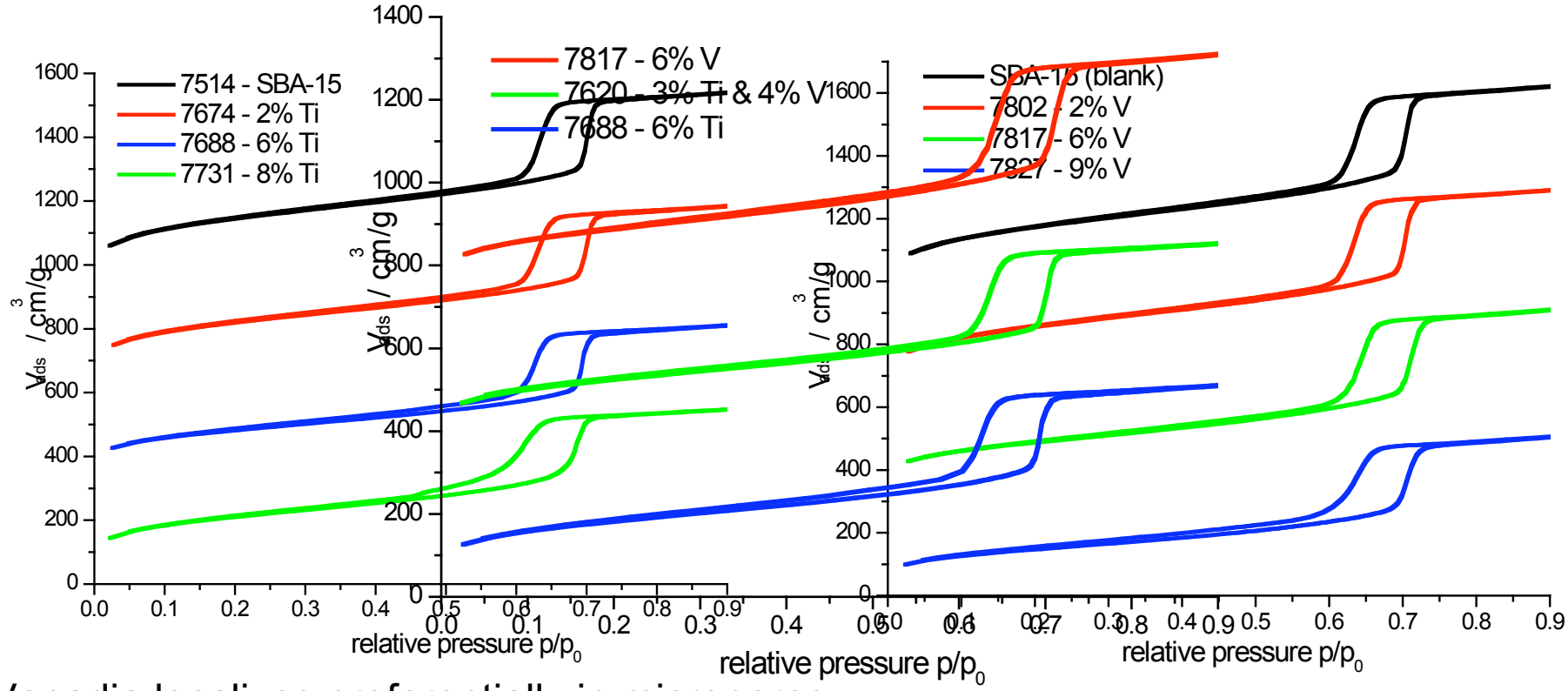
- Synthesize families of title catalysts in reproducible and large quantities.
- Characterize geometric and electronic structures.
- Share with K. Dinse for in-depth electronic structure analysis by EPR.
- Share with R. Schomäcker for kinetic testing.
- Compare with other systems in C3 ODH.
- Identify generic data for comparison with theory.

sample	% wt V set	% wt V from EDX	% wt V from XRF	BET surface / m²/g (16.2nm2/N_2	S(micropore) [m^2/g]	XRD	S(micro)/S(BET)	DFT (equ.) pore size d_0	a0 [nm]	wall tickness [nm]
sample	% wt Ti/V set	% wt Ti from EDX / XRF	% wt V from EDX / XRF	BET surface / m²/g (16.2nm2/N_2)	S(micropore) [m^2/g]	XRD	S(micro)/S(BET)	DFT (equ.) pore size d_0 [nm]	a0 [nm]	wall tickness [nm]
7495	0/0			978	427	no peaks	43,7%	7.59	11.22	3.63
7569	3/0	“3.4“/ 3.45		823	316	no peaks	38,4%	7.31	10.97	3.66
7606	3/0.8	“3.4“/ 3.29	0.98	761	293	no peaks	38,5%	7.31	10.96	3.65
7620	3/4	3.4	3.9	629	192	no peaks	30,5%	7.31	10.94	3.63
7622	15/0	“7.5“/ 8.83		809	292	no peaks	36,1%	7.03	10.96	3.93
7624	15/4	7.5	3.6	319	79	no peaks	24,8%	7.03	10.84	3.81
7841	20	13,0	13.66	200	39	Peak 22.6°	“19.5% ”	Macro poren		

Structural integrity



Textural integrity



Vanadia localizes preferentially in micropores

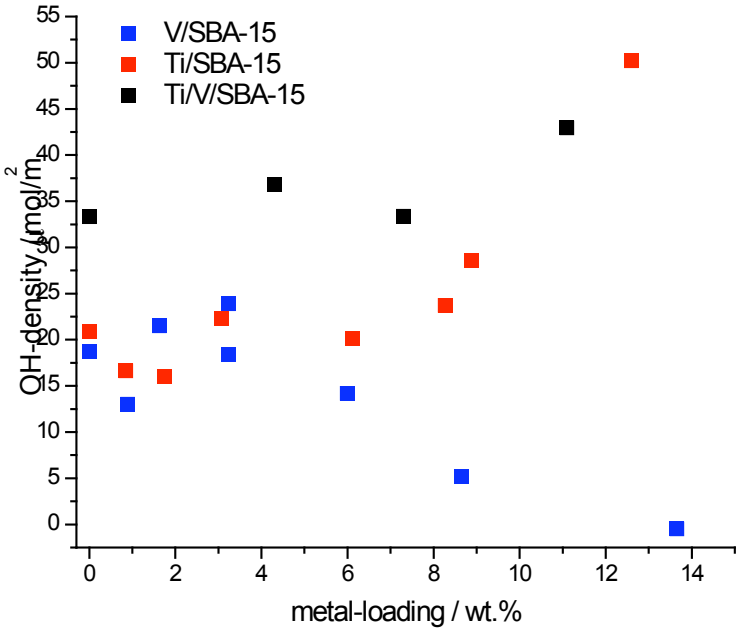
Titania localizes on massive wall parts

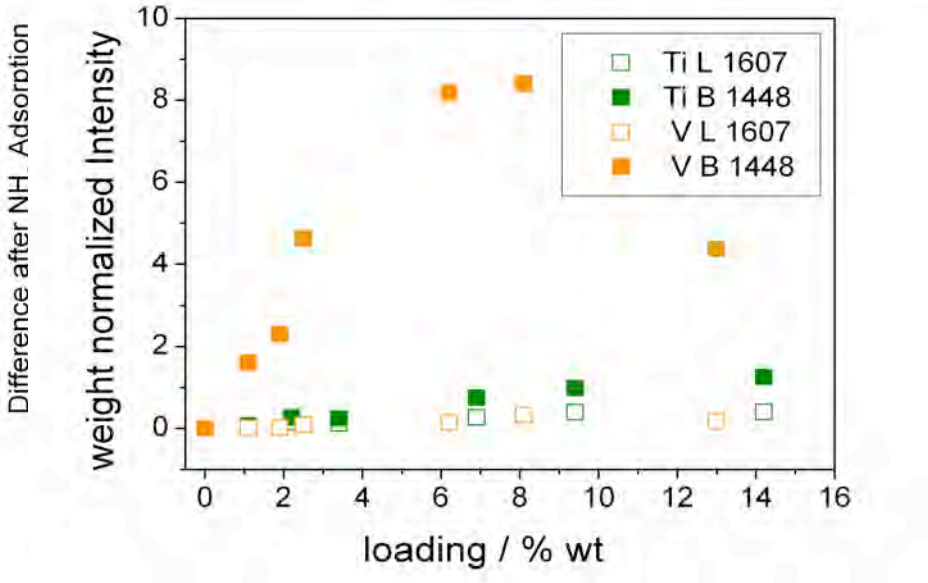
V on Ti localizes substantially on Ti

Integrity of pore system maintained

Crystallization of oxides easily detected (not shown)

OH groups and acid-base chemistry



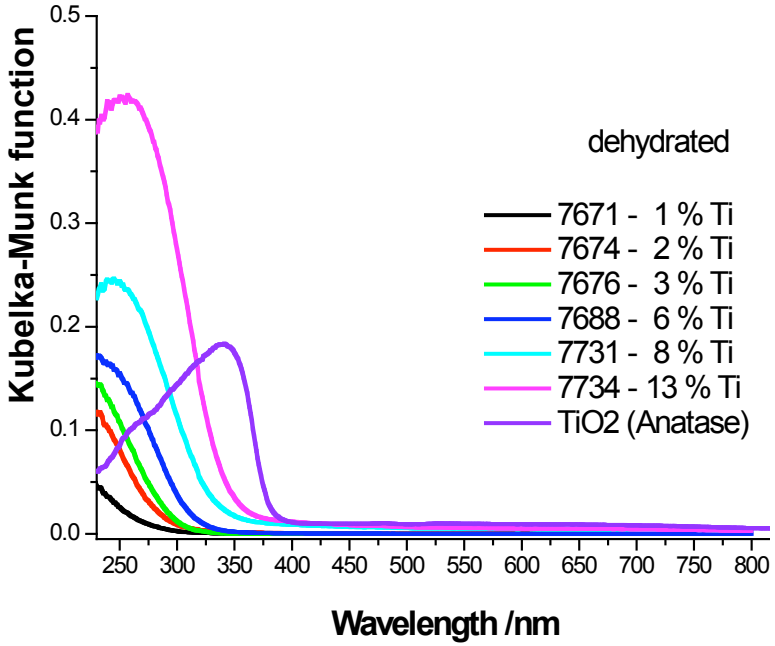


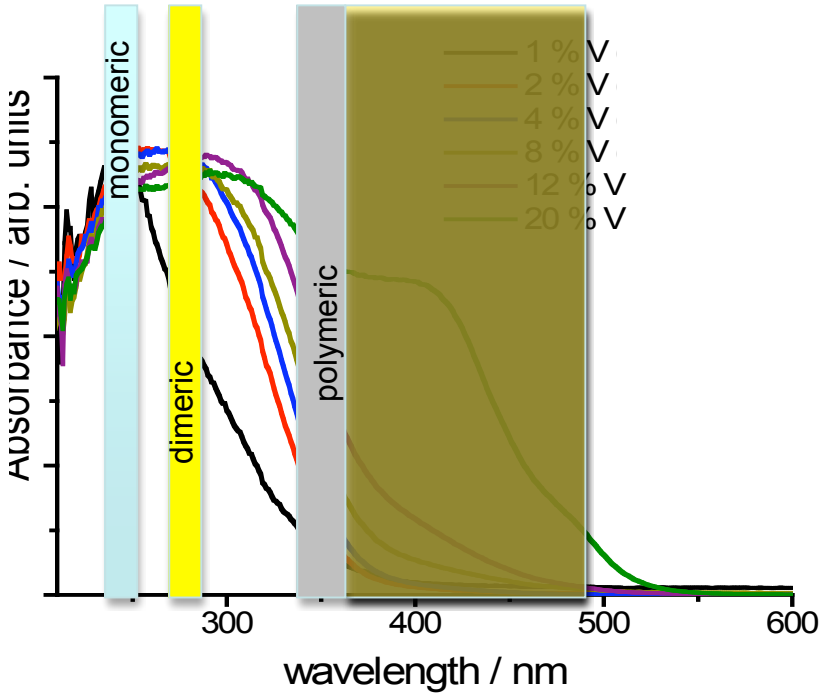
V reacts with all OH groups available (micropores!)

Ti adds more OH groups to the system

Metal loading creates acidity.
Ti-bonded OH weakly acidic.
V-bonded OH strongly acidic.

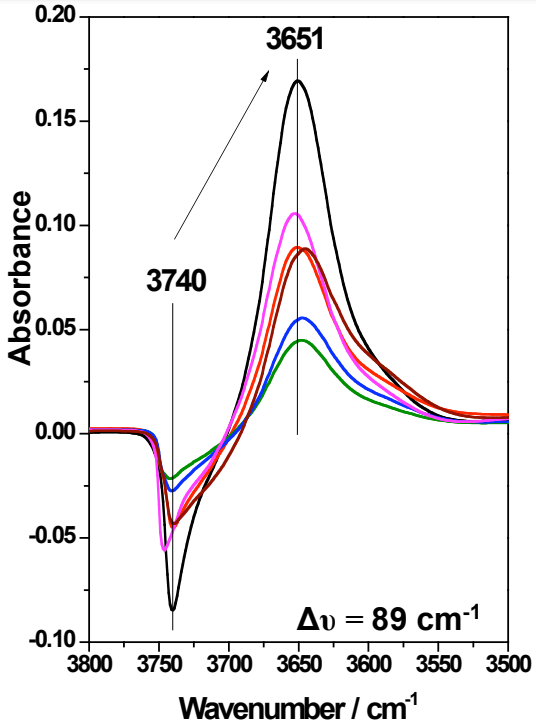
Structure and the metal species





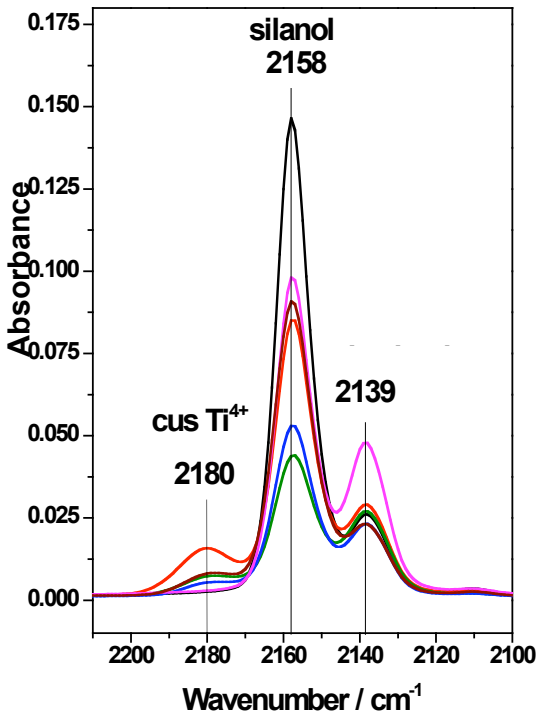
Titania forms tetrahedral distorted species at all loadings (NEXAFS)
Vanadia oligomerizes with increasing loading to a mixture of species (NEXAFS, K.Hermann)
The combination of V+Ti suppresses the structural dynamics of V and leads to mixed oligomers.

Structure of the metal species

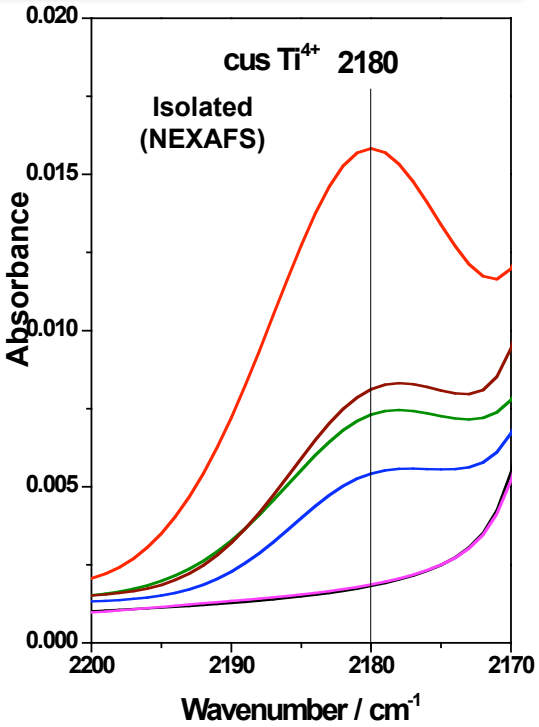


77 K, 0.04 mbar

Hadjiivanov, Applied Catalysis A: General 188 (1999)355-360

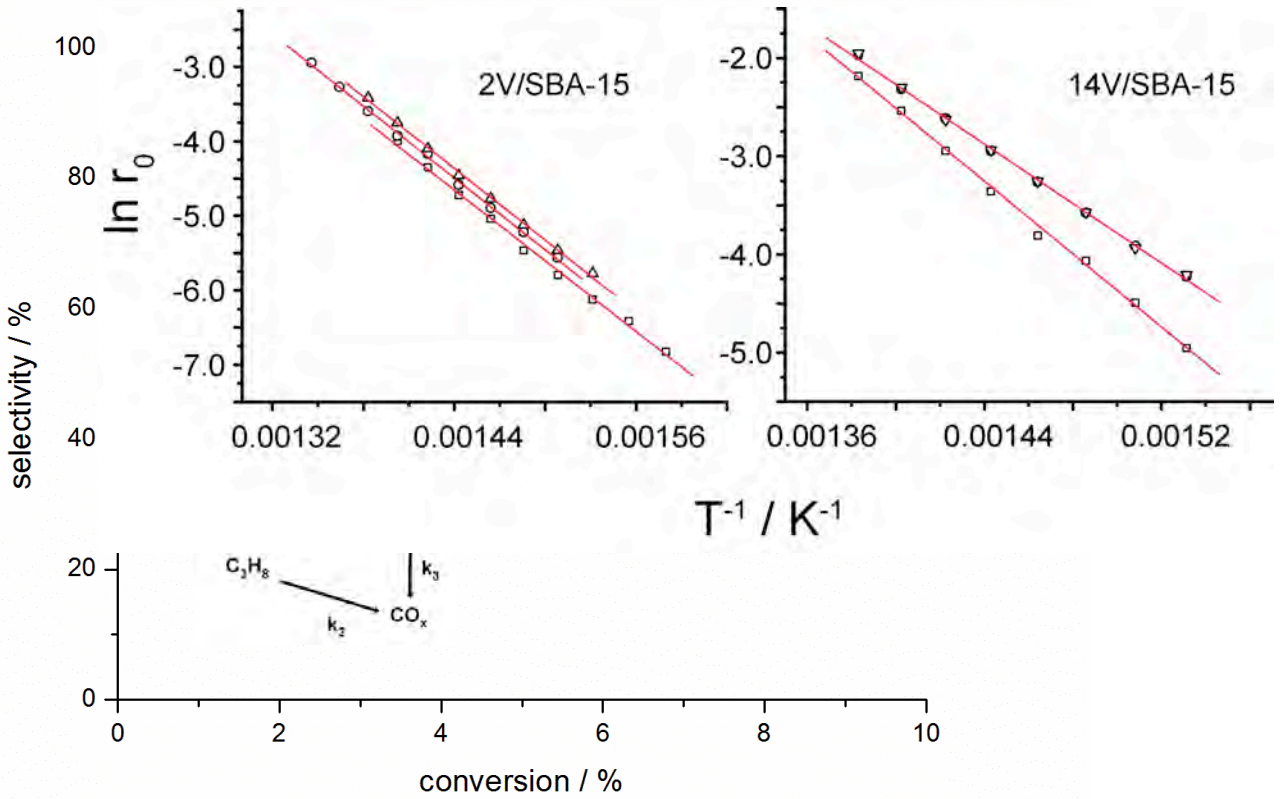


SBA-15, #7495, 0.044 mbar
8Ti/SBA-15, #7622, 0.044 mbar
4V/8Ti/SBA-15, #7624, 0.040 mbar
4V/3Ti/SBA-15, #7620, 0.041 mbar
0.8V/3Ti/SBA-15, #7606, 0.047 mbar
4V/SBA-15, #7815, 0.042 mbar



Anchoring of V on Ti but no coverage:
Non-planar arrangement, micropore location of V.

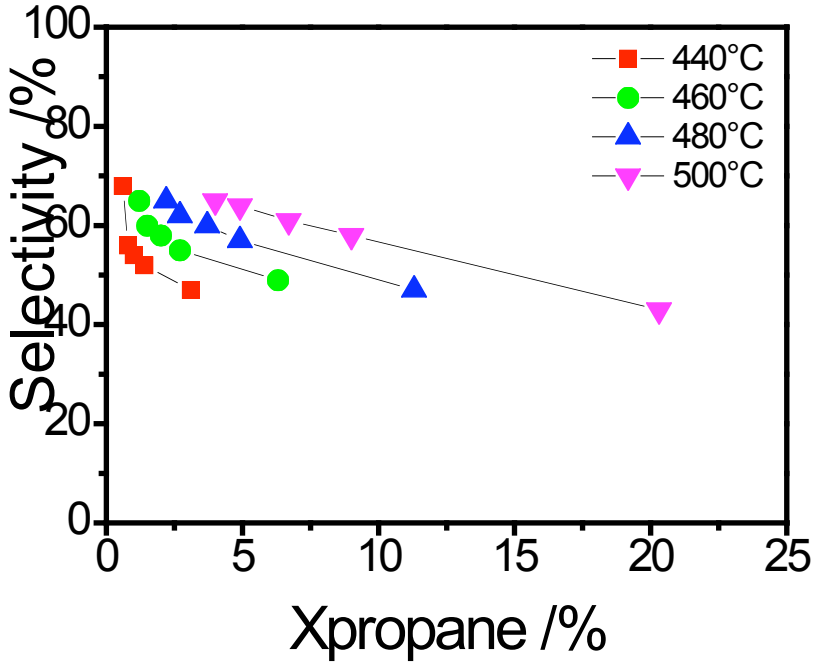
Catalysis



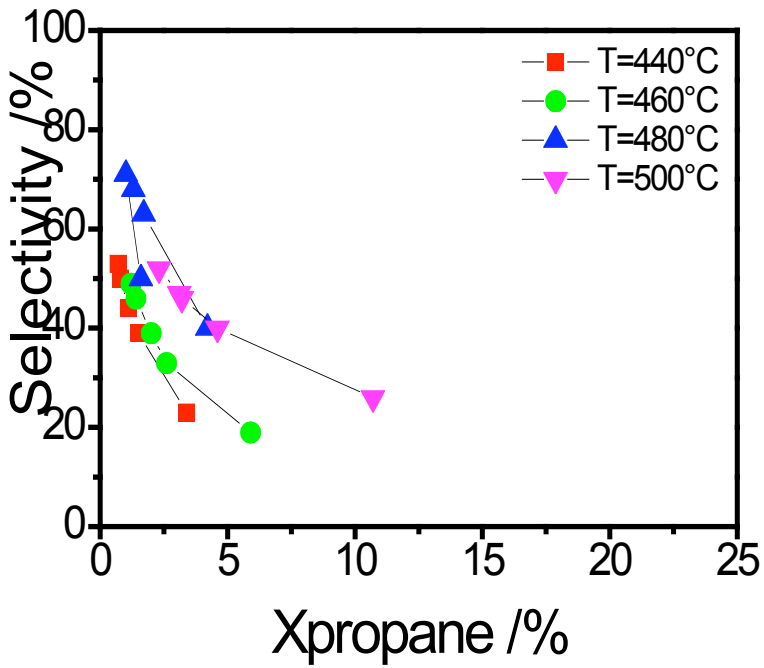
The system is structurally stable at very low loading but becomes gradually dynamical at higher loading

Catalysts:VOx/SBA15

2%VOx/SBA15

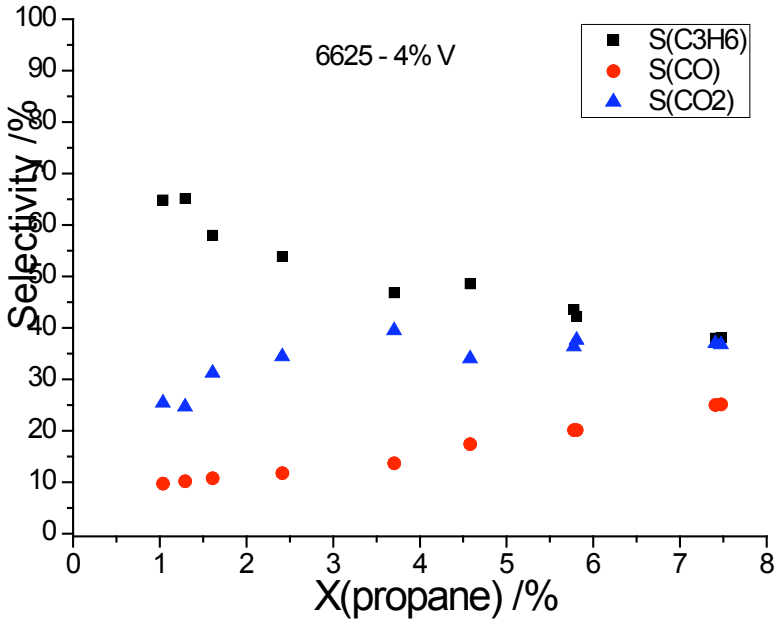


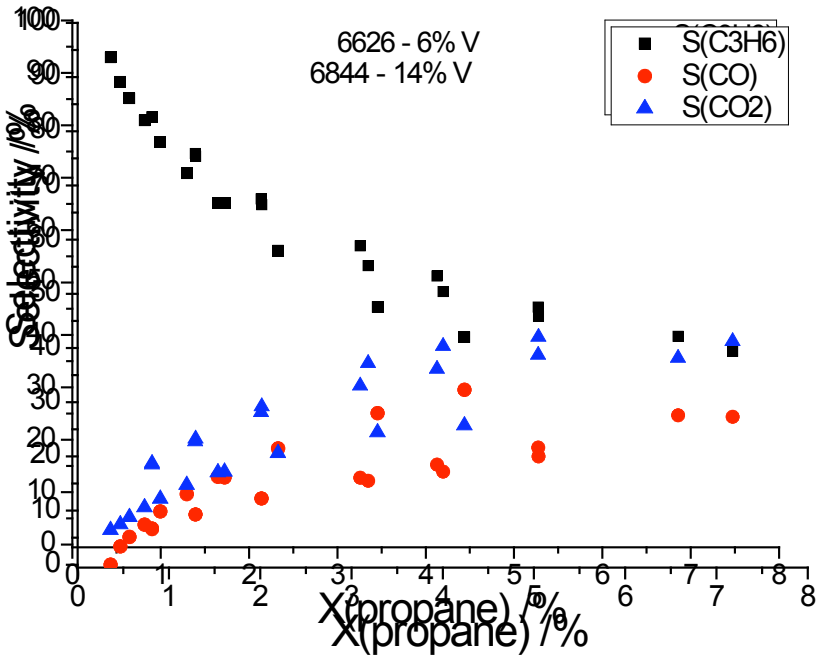
13%VOx/SBA15



Selectivity-conversion trajectories for 2%VOx/SBA15 and 13 VOx/SBA15 catalyst. $C_3H_8/O_2/N_2$ = 17.2/8.6/34.3. Catalysts mass = 300 and 30 mg Flows = 20- 100 cc/min

Multiple reaction pathways: “simple” reaction network?



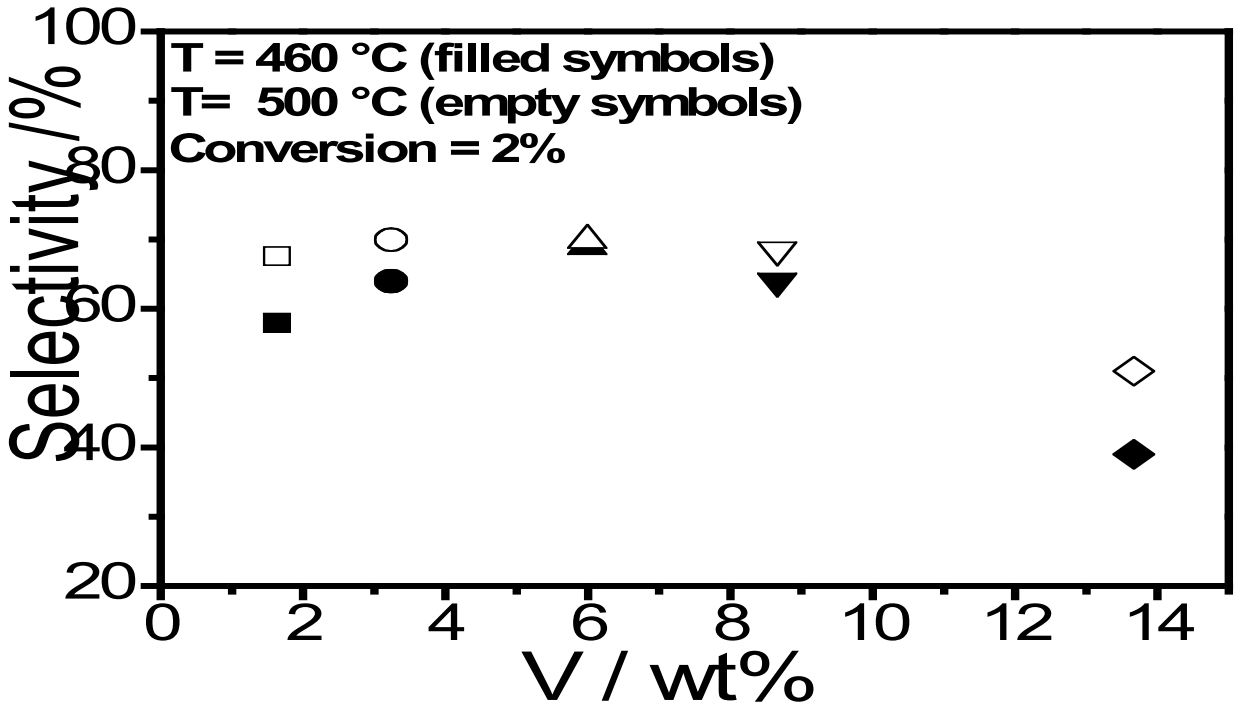


Different loadings (differing species distributions) exhibit in the details of their conversion-selectivity profiles substantial differences:

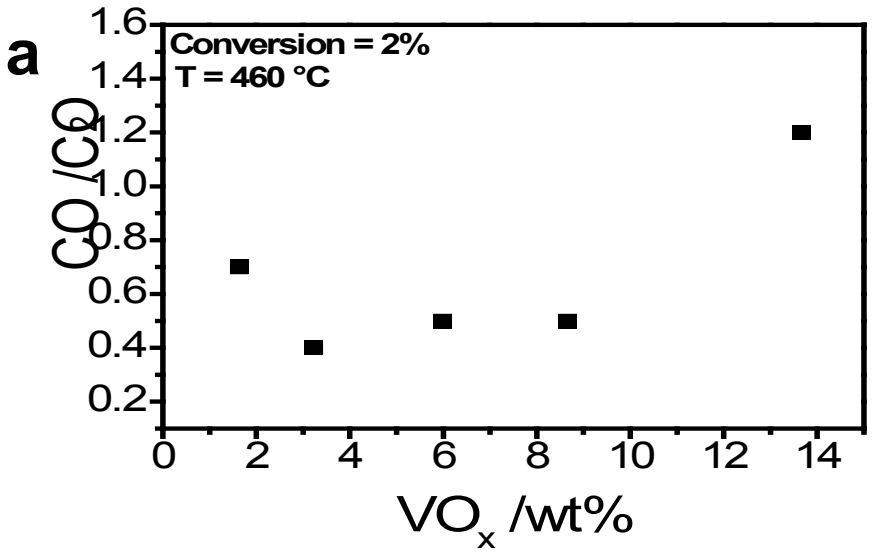
mulitiple sites in action

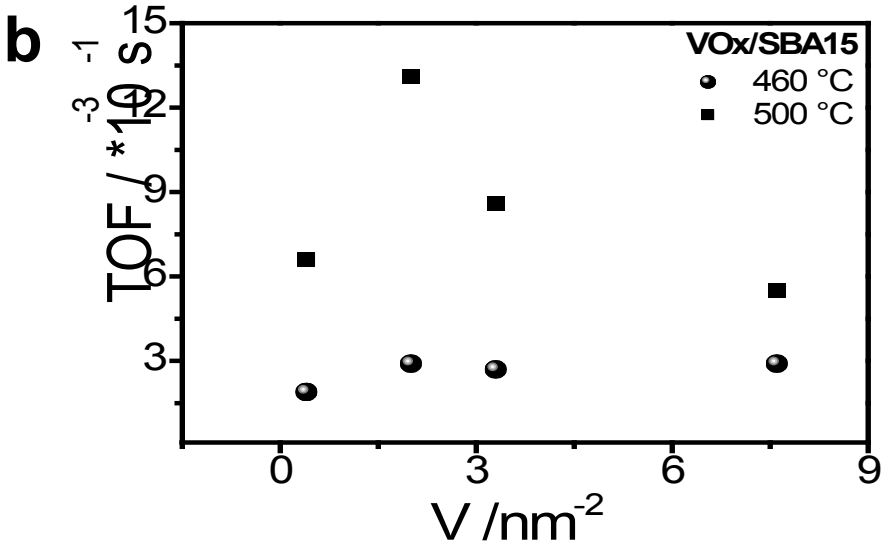
The “noise” in some catalytic data arises from the species interconversion (structural dynamics) with time constants of the catalysis experiments.

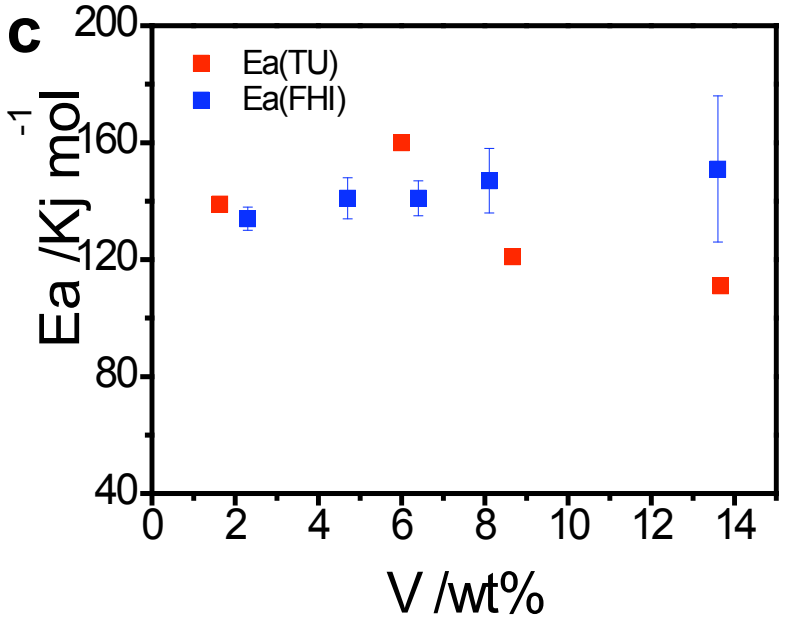
Catalyst: VOx/SBA15



Selectivity fixed at 2 % of conversion for VOx/SBA15 catalysts at 460 and 500°C. C3H8/O2/N2 = 17.2/8.6/34.3 Catalyst mass= 30- 300mg. Flows= 20 – 100 ml/min.





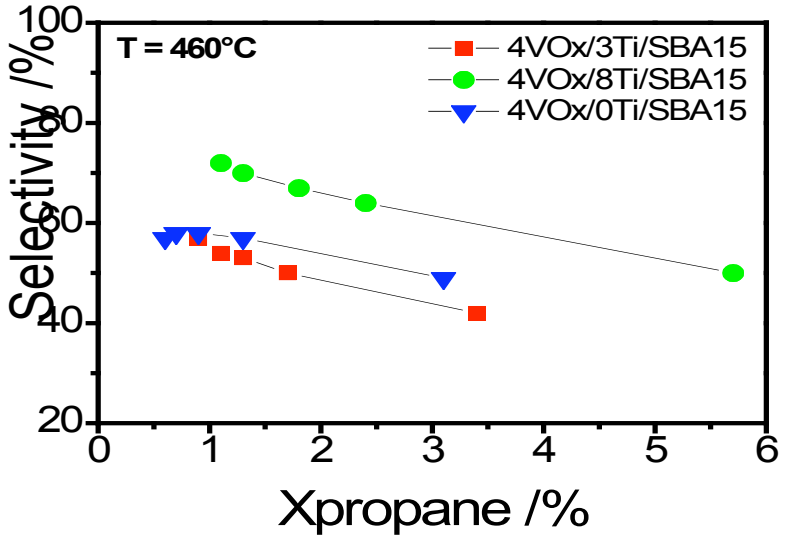


CO/CO_2 ratio **(a)** TOF **(b)** and activation energy **(c)** as a function of the vanadium loading. $C_3H_8/O_2/N_2$ = 17.2/8.6/34.3 Catalyst mass = 30 – 300 mg.

Flows = 20 – 100 ml/min.

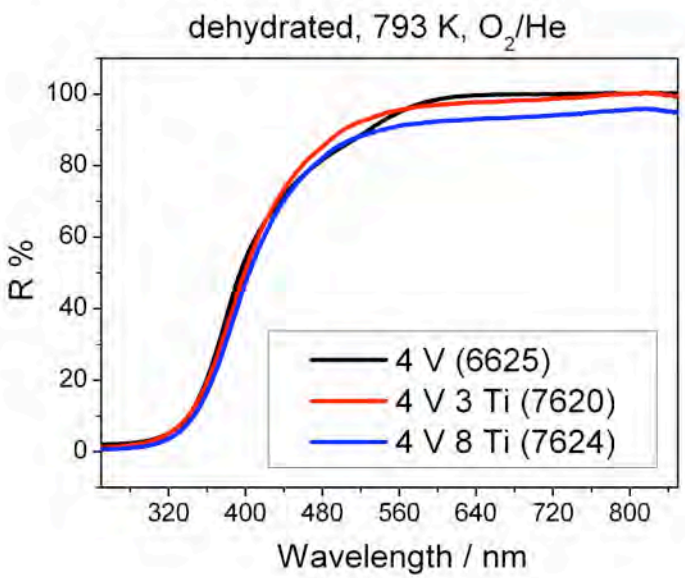
Catalysts:VOx/Ti/SBA15

"Grading" of catalysts
depends much on conditions!



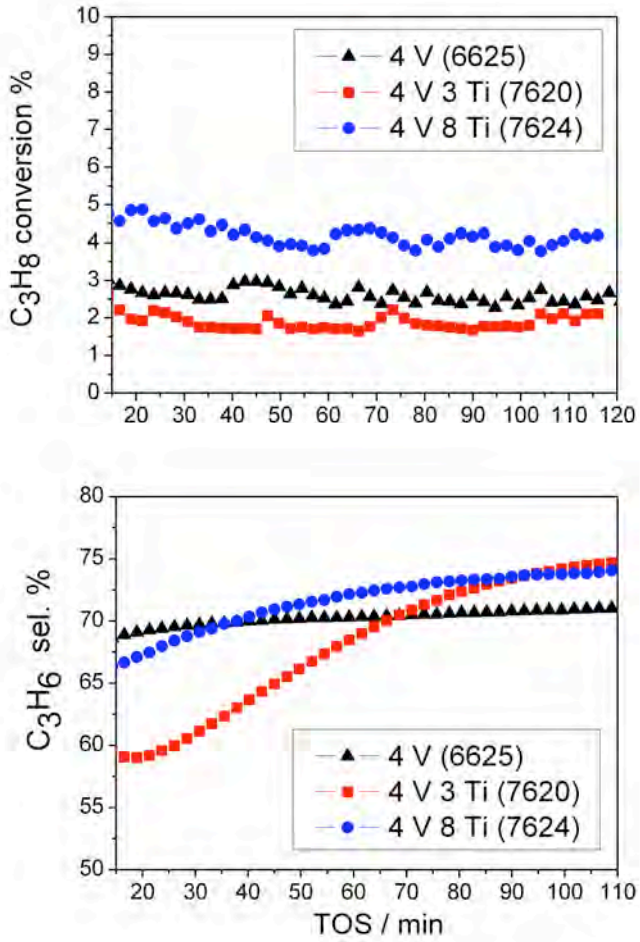
$C_3H_8/O_2/N_2$ = 17.2/8.6/34.3. Catalysts mass = 300 and 30 mg. Flows = 20- 100 cc/mi

Electronic structure and reactivity

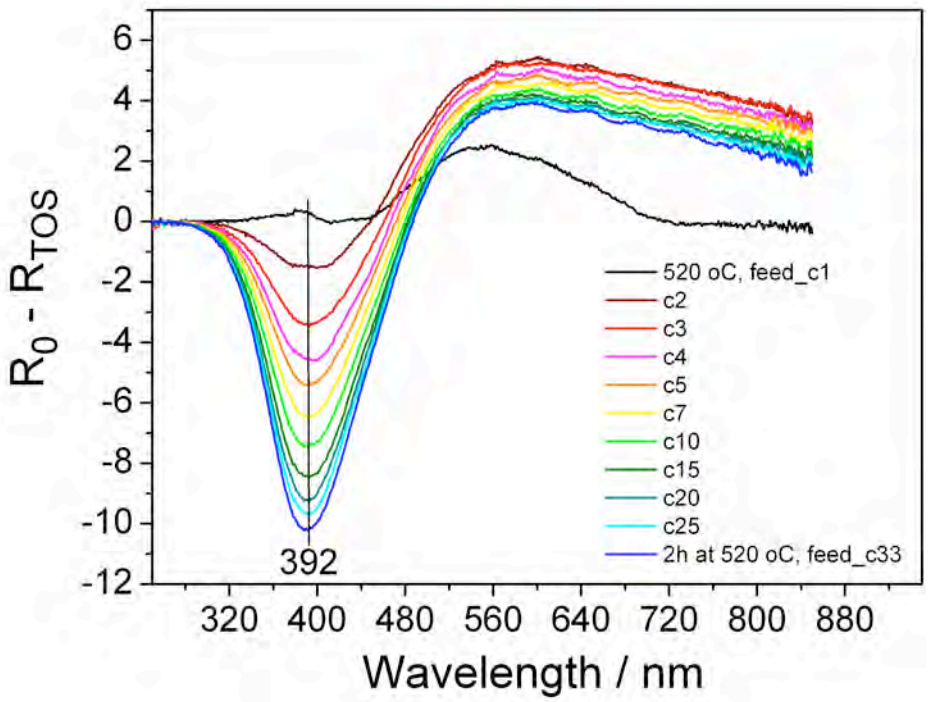


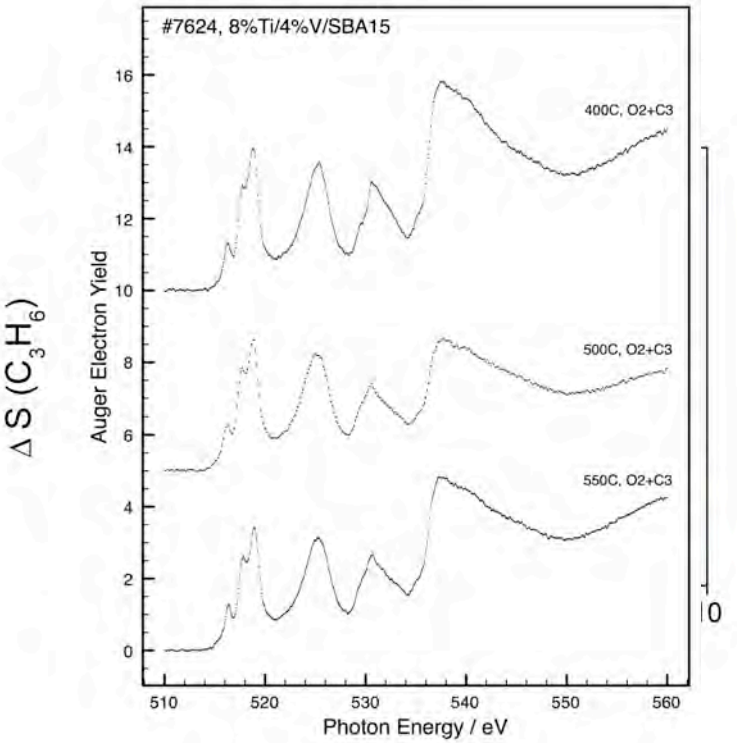
In-situ UV-Vis reveals similar initial electronic structure of the V species:

In feed a differentiation occurs reflecting the presence of the Ti species.



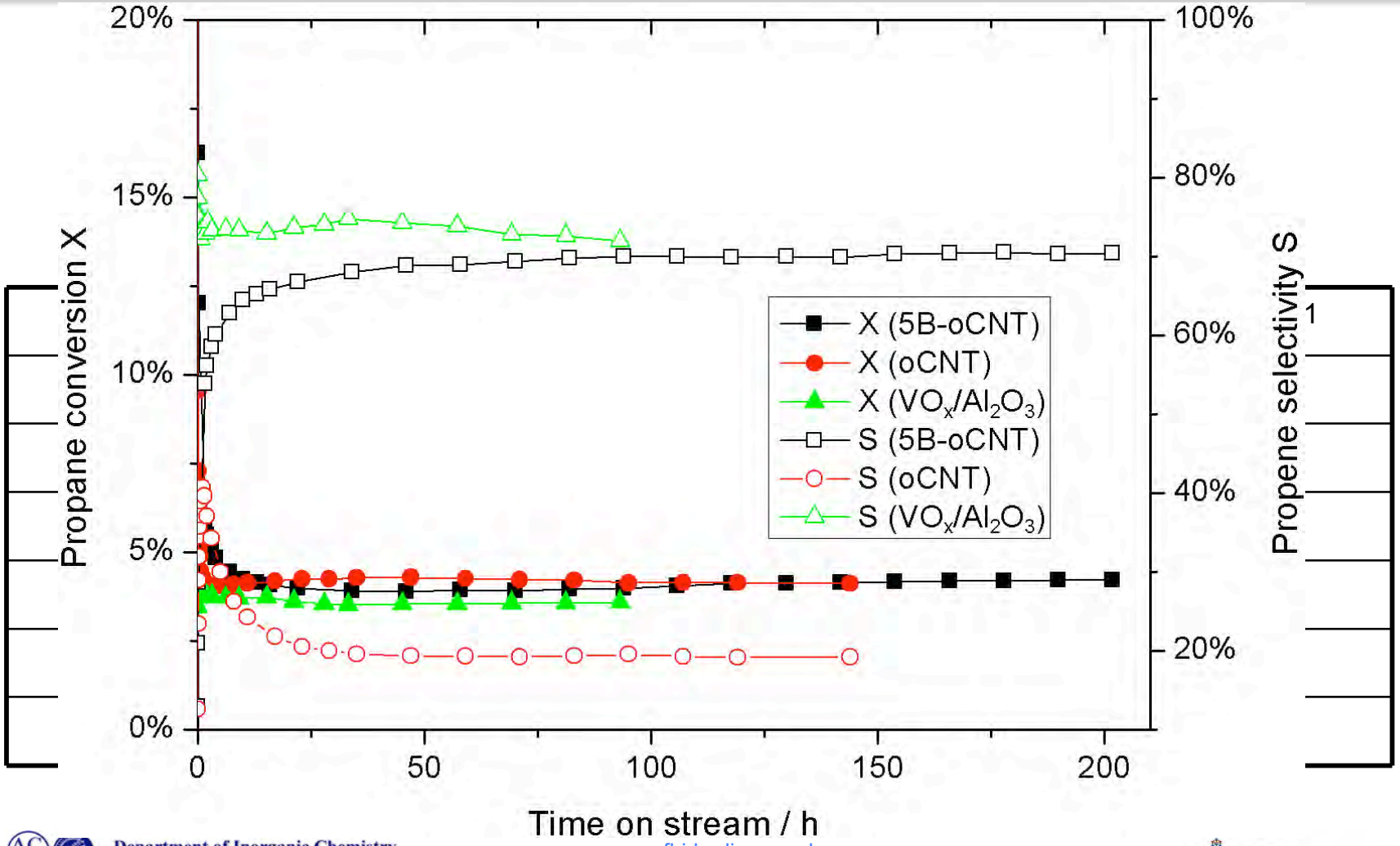
Structural dynamics



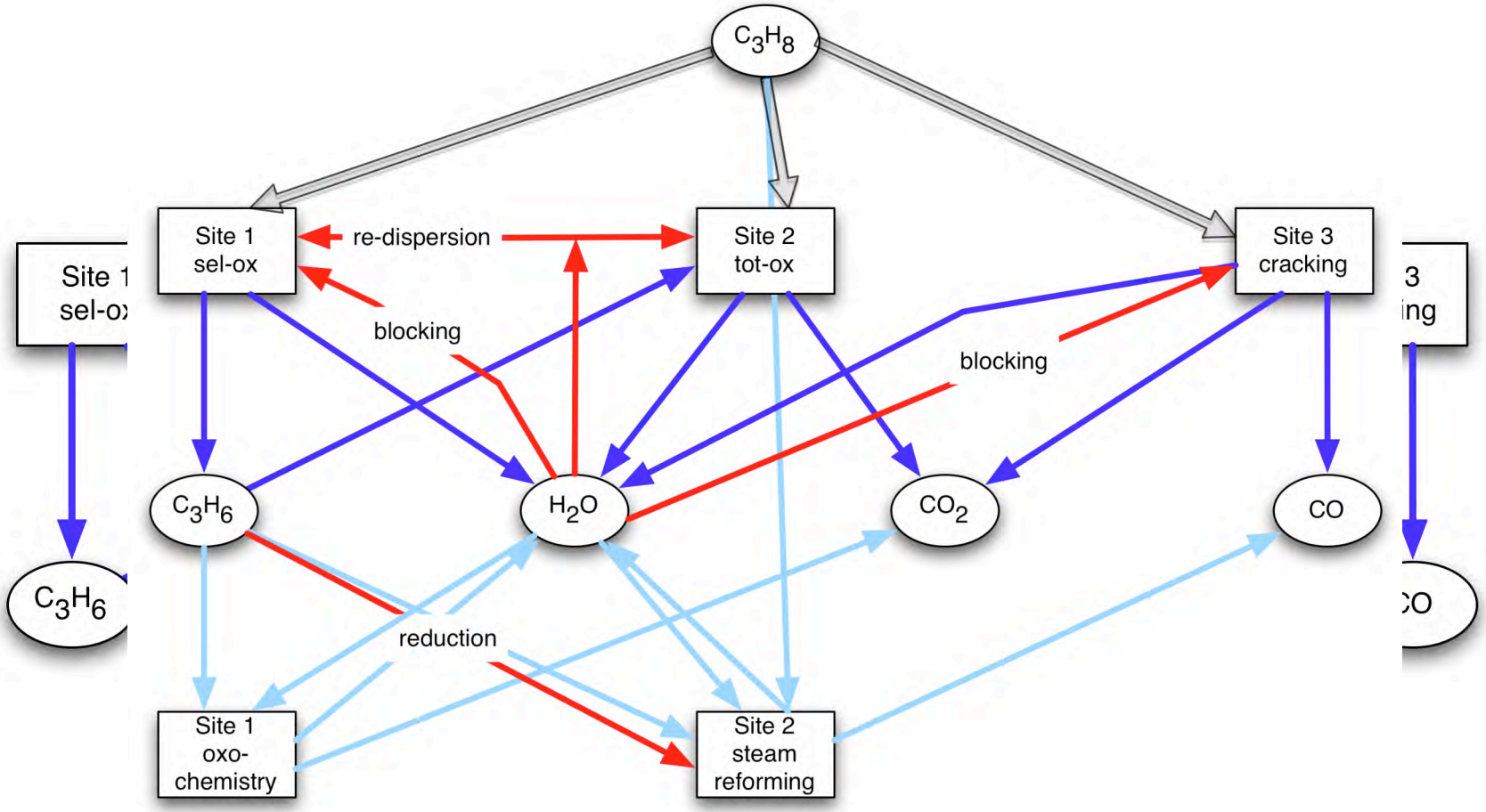


The catalyst becomes more selective when
The species at 392 nm (larger V-O-V arrays (RAMAN)) disappear; The reducibility (d-d-transitions) remains limited.
In NEXAFS spriting of V on Ti is detected, the average oxygen coordination changes.

Reaction rate constants for C3 ODH



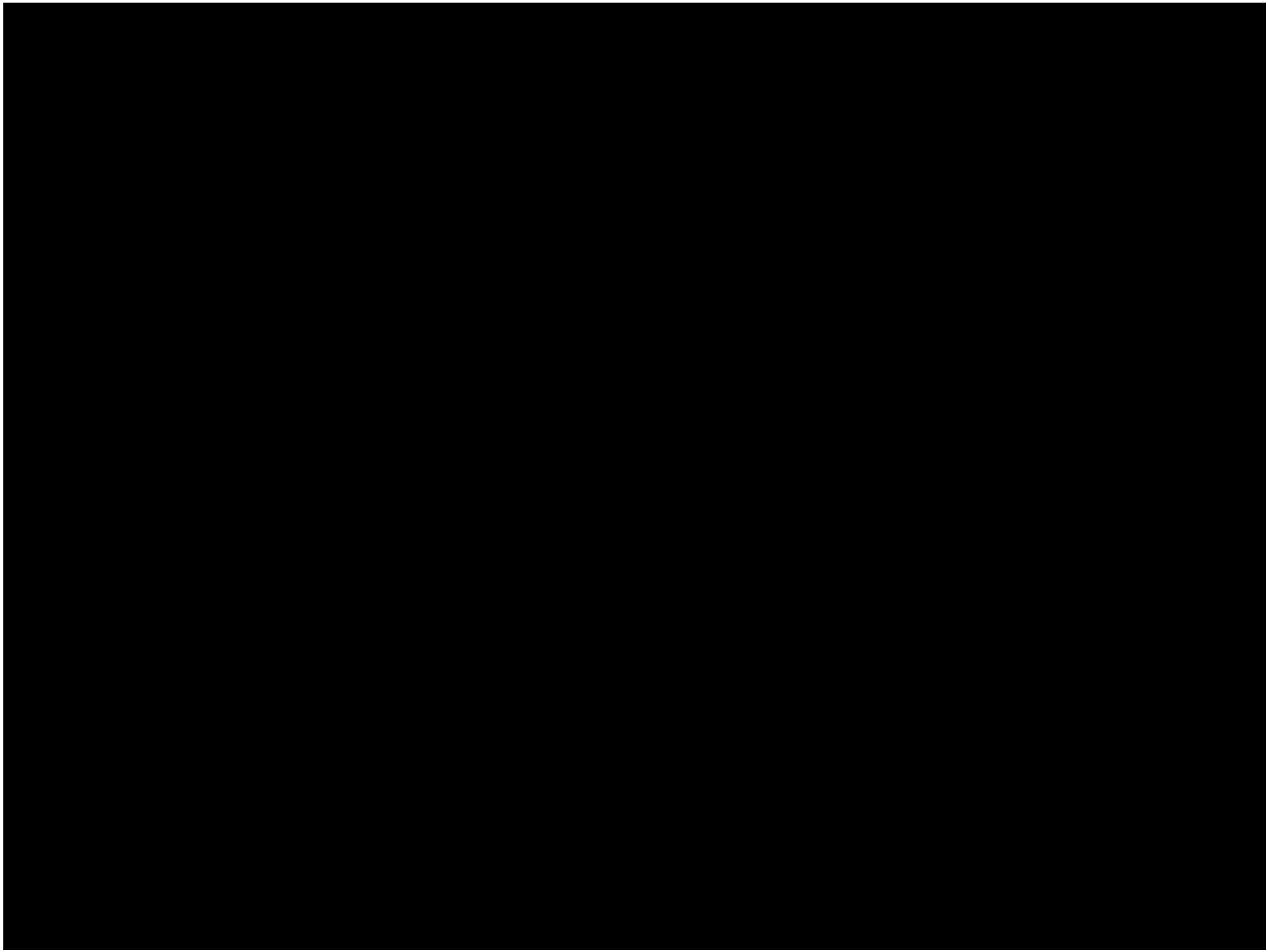
A reaction network



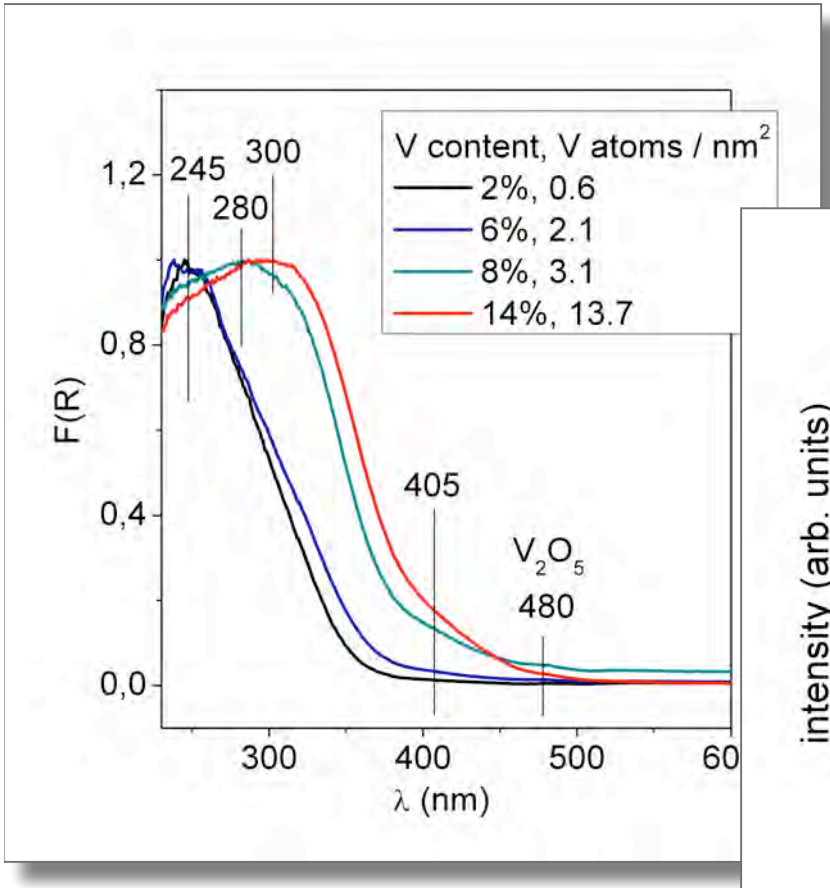
Results and future activities

- V is dynamical.
  - Static diluted and static crystalline are not desired.
  - Rapid dynamics is detrimental.
  - Redox dynamics requires an optimum.
- Multiple active sites for different reactions: kinetic parameters are intermixed.
- Beware of tof!
- Ti (mixed species) suppresses polymeric species and its mobility.

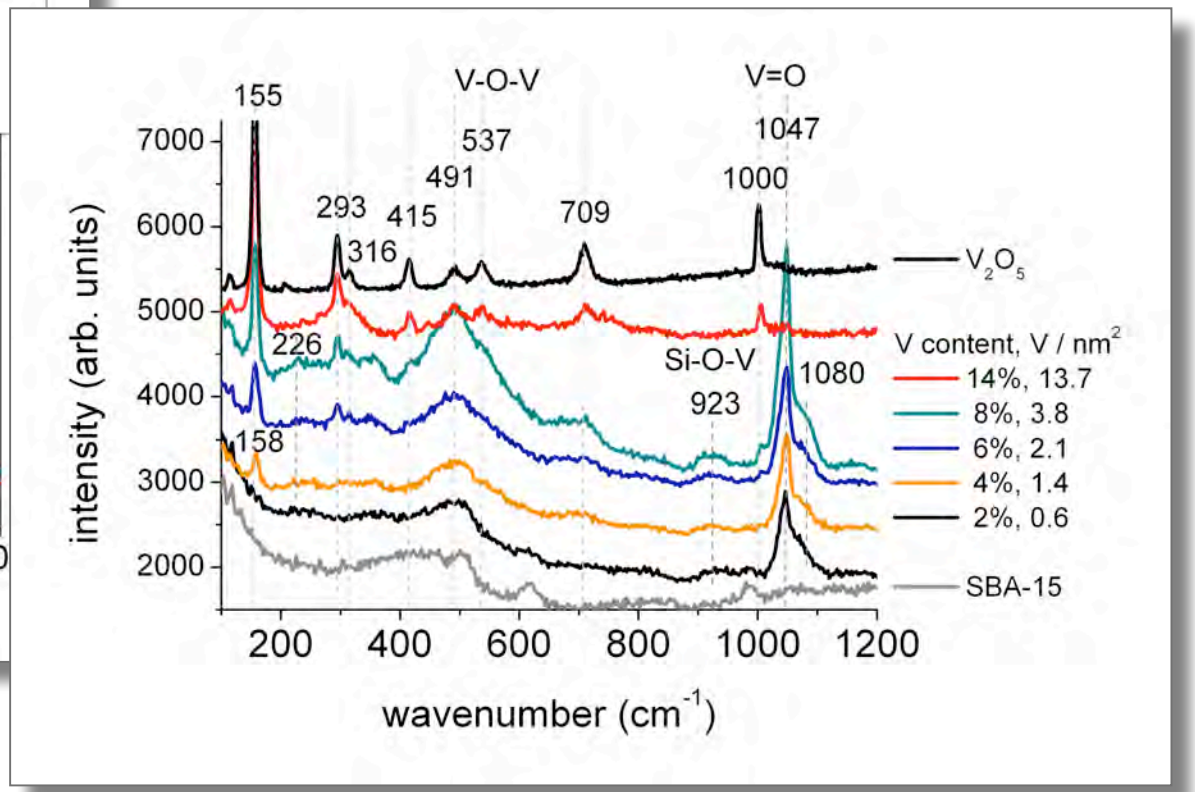
- Gas phase chemistry?
- CO_x chemistry.
- Kinetics of temporal changes.
- Complete Ti/V matrix.
- Create Ce/V matrix.



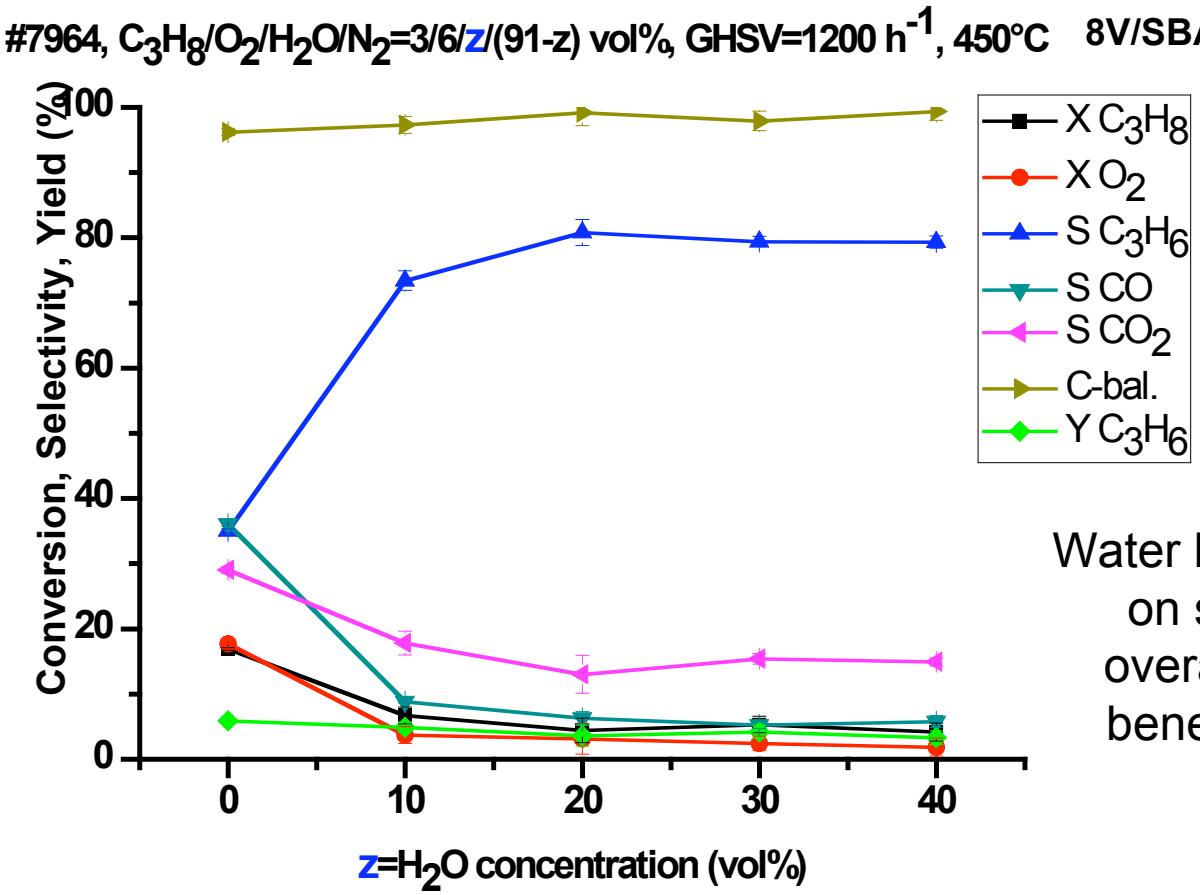
Structure of the metal species



UV-Vis and RAMAN are differently sensitive to the aggregation and coordination of the metal species



Process under severe conditions



Water has a different effects on several site types: overall site blocking but beneficial for selectivity