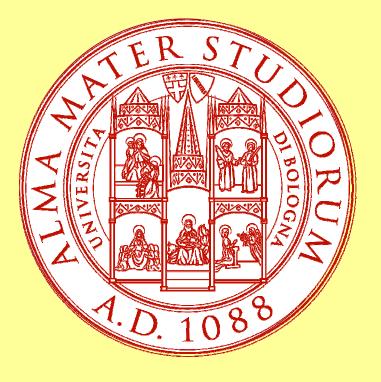


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Members of the EU-funded Coordination Action of Nanostructured Catalytic Oxide Research and Development in Europe (CONCORDE)

# Structure-reactivity relationships in supported VO<sub>x</sub> catalysts for the selective oxidation of 1-butene to acetic acid: A comprehensive in situ-study

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#### Introduction and Objectives

#### Conclusions

The industrial manufacture of ethylene and propylene is based on naphtha cracking. Side products of this process are n-butenes and n-butane which are usually re-fed to the reactor. Oxyhydrating scission of these molecules to acetic acid (AA) is a promising way for their valorization. However, the performance of supported vanadium oxides being the best catalysts so far must still be improved, in particular with respect to n-butane conversion. This goal is only met by understanding precisely how the nature of active V sites (redox behaviour, dispersion, coordination) is influenced by support properties and synthesis conditions. Therefore, we have studied a variety of VO<sub>x</sub> catalysts differing in the nature of the support, the V loading as well as in the preparation procedure under reaction-like conditions using 1-butene as model compound by different in situ-methods (EPR, UV/VIS-DRS, FTIR).

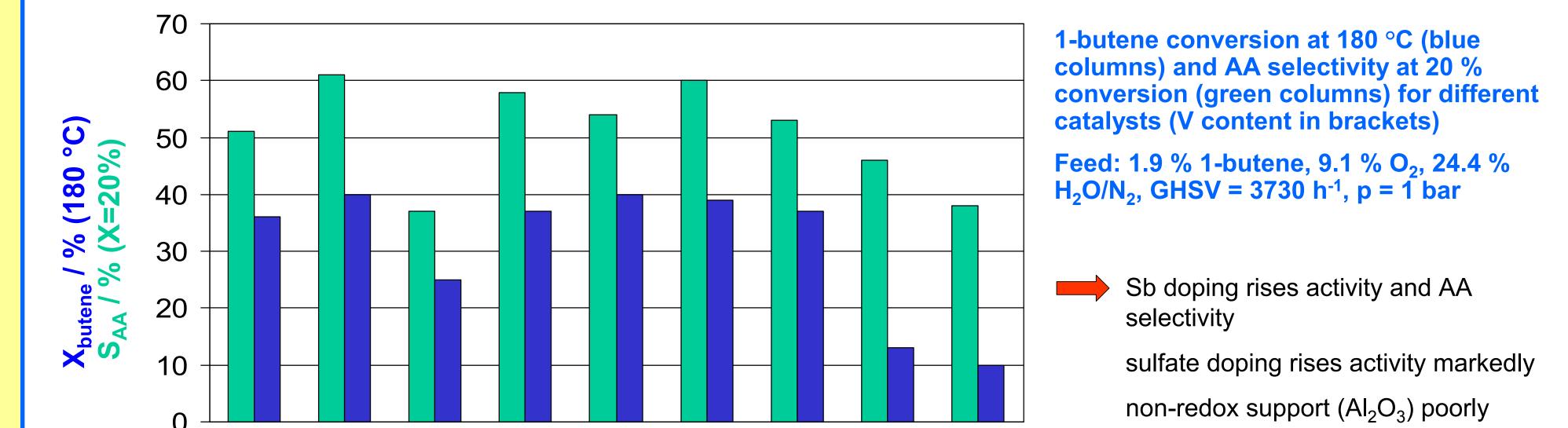
- >  $VO_x$  on  $SO_4$ -containing anatase is most effective while  $VO_x$  on non-reducible  $AI_2O_3$  is poorly active.
- > Activity is governed by highly dispersed VO<sub>x</sub> surface species while  $V_2O_5$  particles seem to be inactive.
- By Sb-doping, a non-stoichiometric amorphous Sb-vanadate is formed that lowers the vanadium redox potential and improves the AA selectivity.
- SO<sub>4</sub>-doping stabilizes active V sites on the catalyst surface, thus, improving the catalytic performance.
- Adding water to the feed improves AA selectivity by favouring the hydrolysis of the ketone intermediate.

## Catalysts

- > spray-drying (SD) of a slurry of sulfate-doped (S)  $TiO_2$ ,  $V_2O_5$ and  $Sb_2O_3$
- impregnating (I) TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with NH<sub>4</sub>VO<sub>3</sub> or VO(acac)<sub>2</sub>

Catalyst	Cryst. phases	V wt%	S <sub>BET</sub> m²/g
Ti,S-SD	Anatase V <sub>2</sub> O <sub>5</sub>	6.1	79
Ti,S,Sb-SD	Anatase Sb <sub>2</sub> O <sub>3</sub>	4.2	74
Ti,S-I	Anatase	1 to 14	60 to 80
Ti-l	Anatase	4.2	70
AI-I	γ,δ-Al <sub>2</sub> O <sub>3</sub>	3.7	61

#### **Results of catalytic tests**

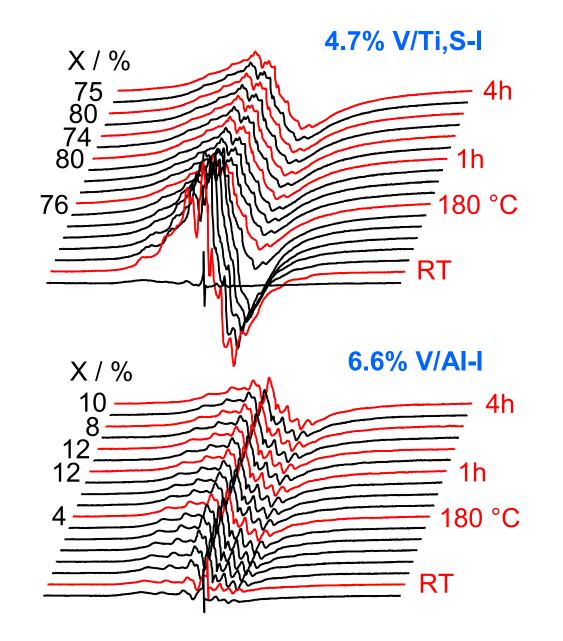


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support	Ti,S	Ti,S,Sb	Ti,S	Ti,S	Ti,S	Ti,S	Ti,S	Ti	ΑΙ
method	SD	SD	I	I	I	I	I	I	I
V content	6.1	4.2	1.1	3.3	4.7	9.7	14.0	4.2	3.7

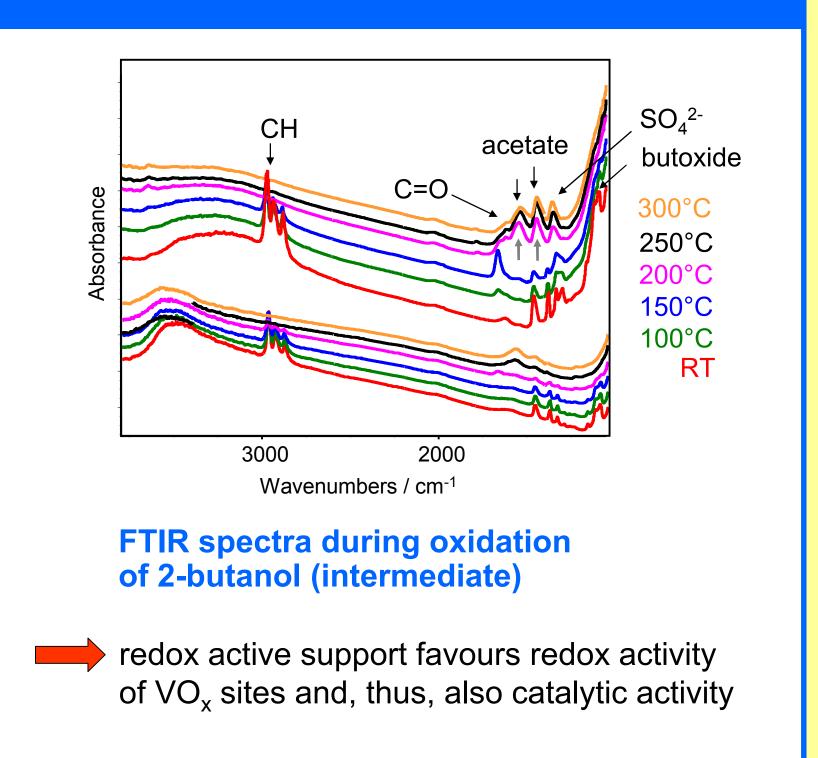
active

increasing V content above 3.3 % leads to no further improvement

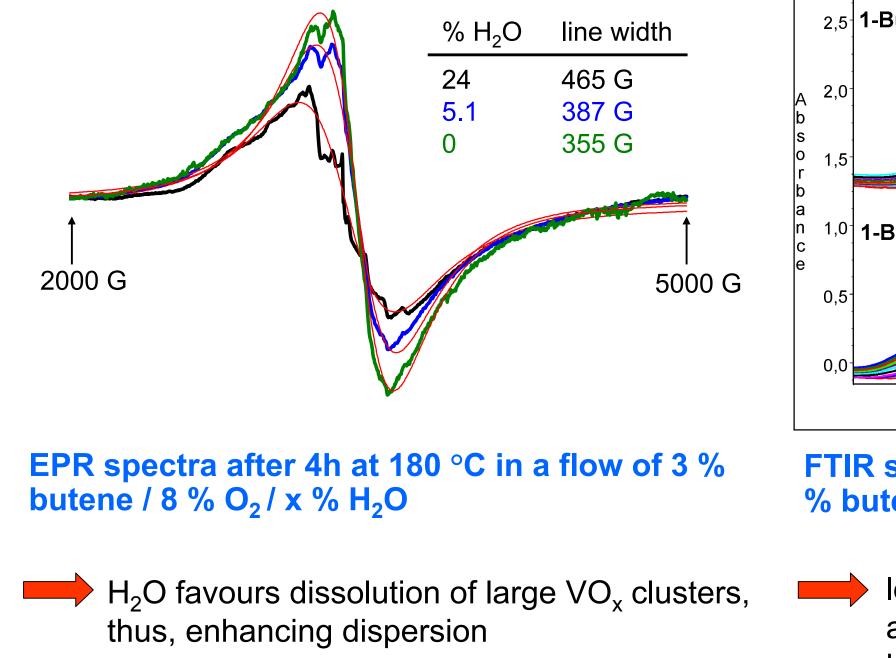
## Influence of support

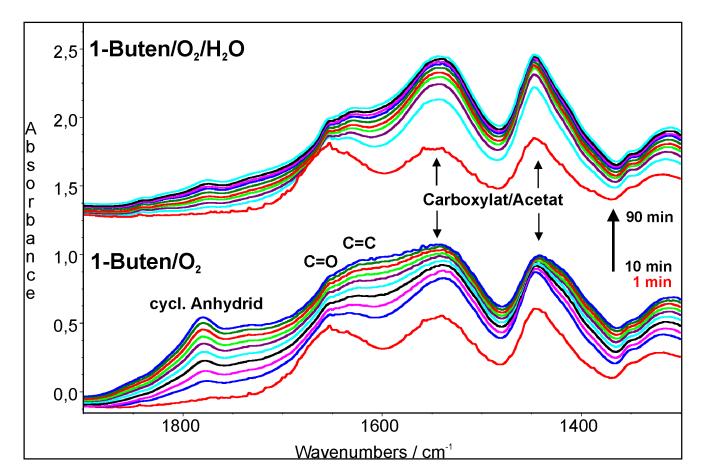


EPR spectra after 4h at 180 °C in a flow of 2 % butene / 9 %  $O_2$  / 24.4 %  $H_2O$ 



## Influence of water (Ti,S-SD)

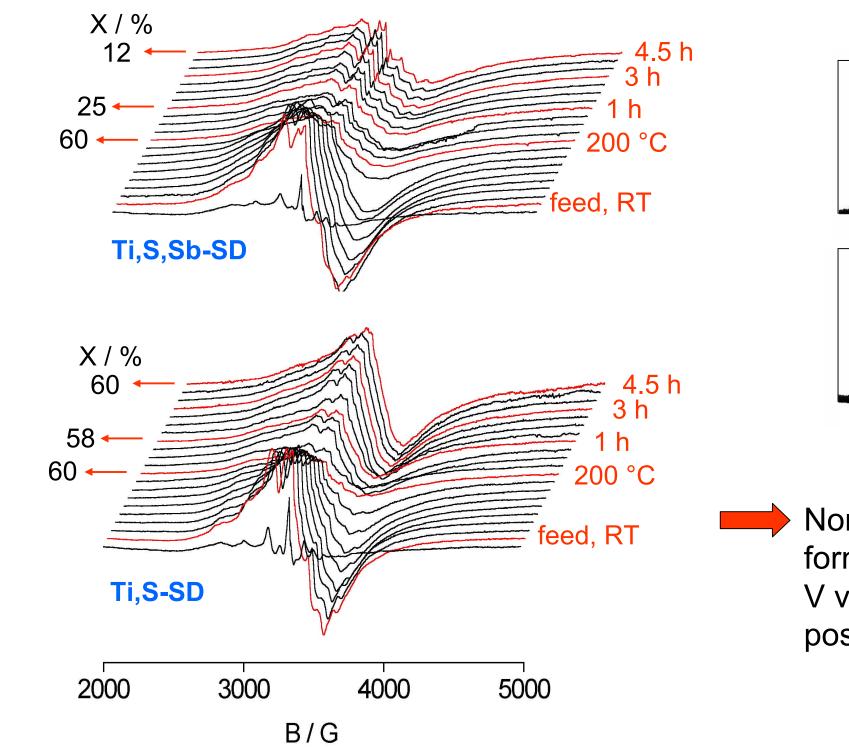


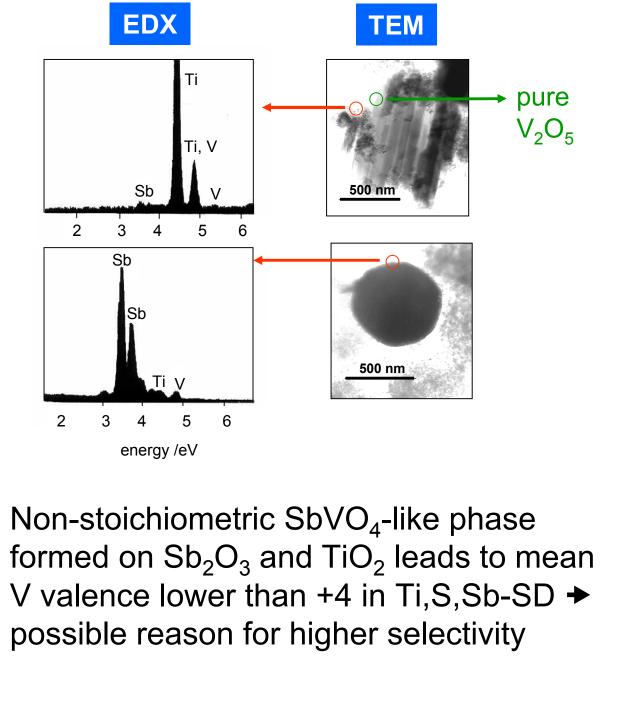


FTIR spectra at 200 °C in a flow of 3 % butene / 8 %  $O_2$  / x %  $H_2O$ 

less cyclic anhydrides in favour of acetate formation by hydrolysis of ketone intermediate

#### Influence of Sb doping





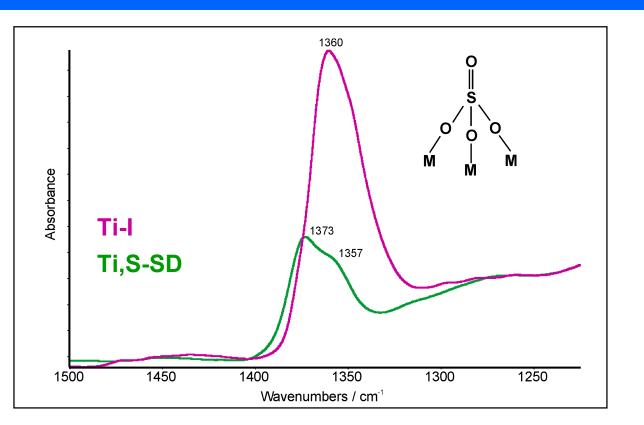
### Influence of sulfate doping

Redox kinetics of V sites followed by UV/VIS-DRS

	reduction in 3% 1-butene/N <sub>2</sub>		reoxidation in 9% O <sub>2</sub> /N <sub>2</sub>		
rate const.	Ti,S-SD	Ti-l	Ti,S-SD	Ti-l	
k <sub>1</sub> / min <sup>-1</sup>	0.172	0.449	0.187	0.076	
k <sub>2</sub> / min <sup>-1</sup>	0.011	0.019	0.016	0.011	

Following the absorbance at 600 nm (d-d transitions of reduced V ) as a function of time at 180 °C

- Two processes (pseudo-first-order)
  1) surface V species (fast)
  2) bulk V species (slow)
- Sulfate-free catalyst faster and deeper reduced, slower and uncompletely reoxidized



FTIR spectra in the v(SO) range of the vanadium free TiO<sub>2</sub> and sample Ti,S-SD

- Intensity loss and shift of v(SO) in the presence of V species
- Sulfate is in direct contact with the V species and may keep them in redox active state on the surface

We thank the Consortium für Electrochemische Industrie München for providing catalysts and the German Federal Ministry of Education and Research and the Senate of Berlin for financial support.