

# 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

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).

## Conclusions

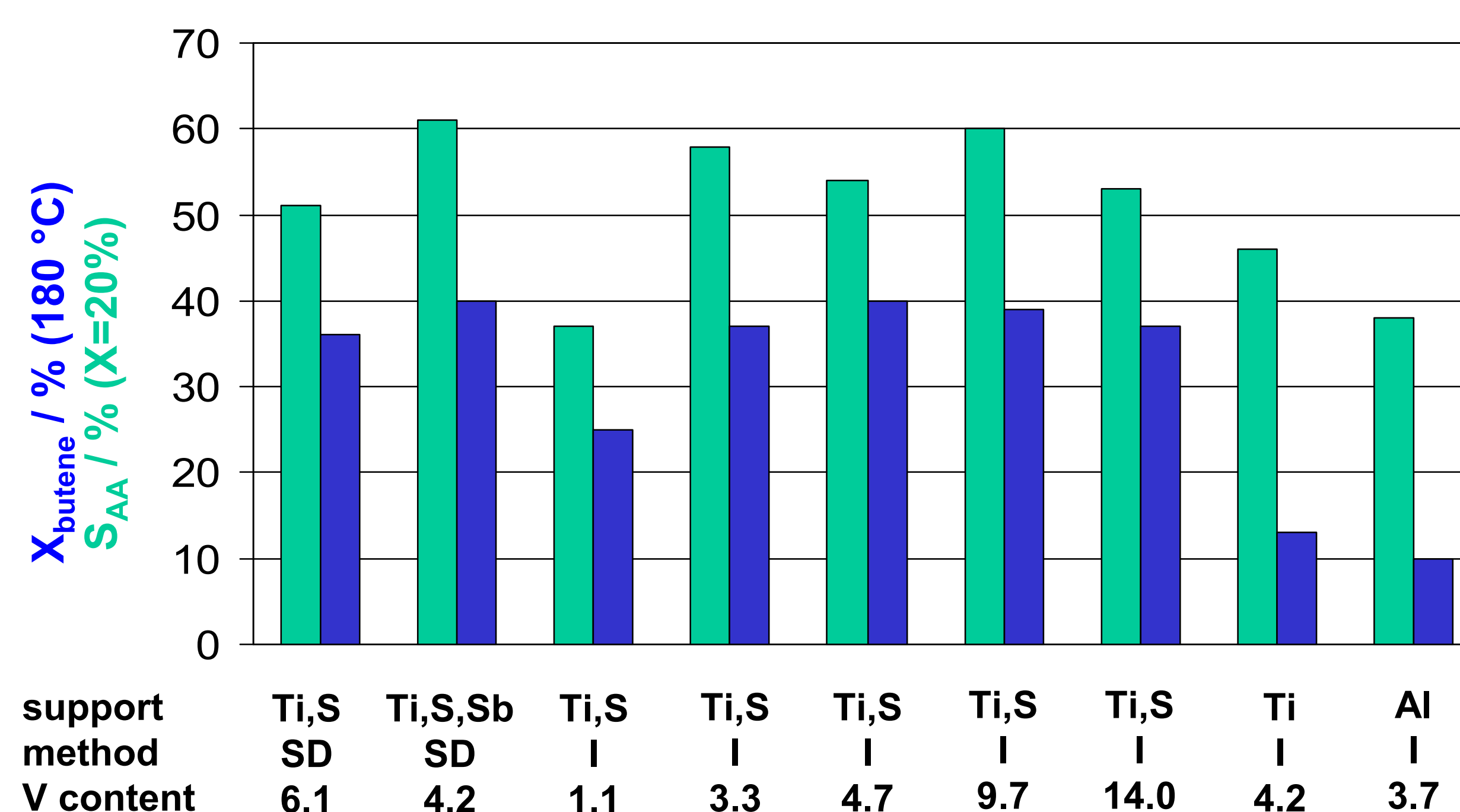
- VO<sub>x</sub> on SO<sub>4</sub>-containing anatase is most effective while VO<sub>x</sub> on non-reducible Al<sub>2</sub>O<sub>3</sub> is poorly active.
- Activity is governed by highly dispersed VO<sub>x</sub> surface species while V<sub>2</sub>O<sub>5</sub> particles seem to be inactive.
- By Sb-doping, 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<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>3</sub>
- 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> m <sup>2</sup> /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-I	Anatase	4.2	70
Al-I	γ,δ-Al <sub>2</sub> O <sub>3</sub>	3.7	61

## Results of catalytic tests

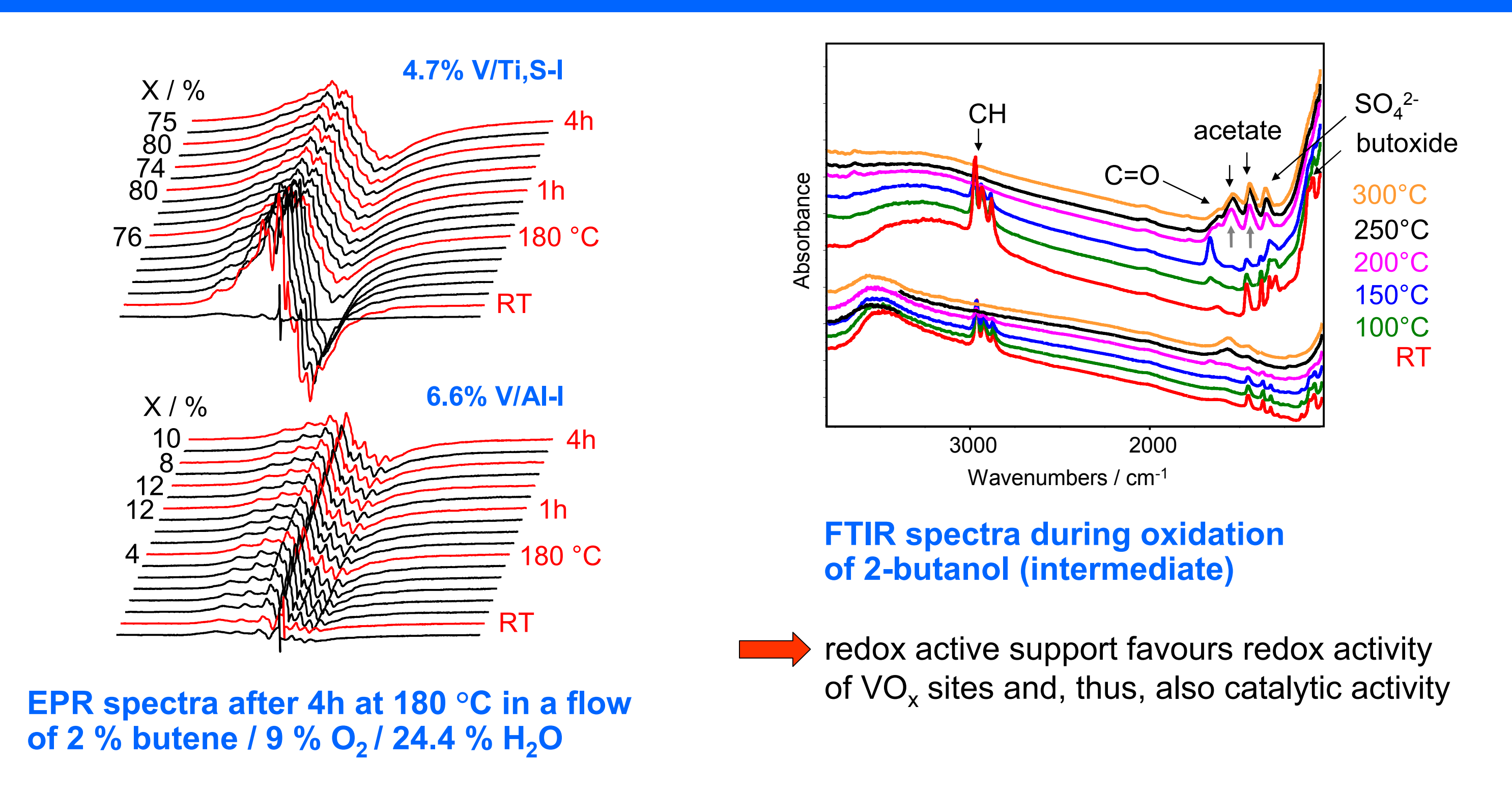


1-butene conversion at 180 °C (blue columns) and AA selectivity at 20 % conversion (green columns) for different catalysts (V content in brackets)

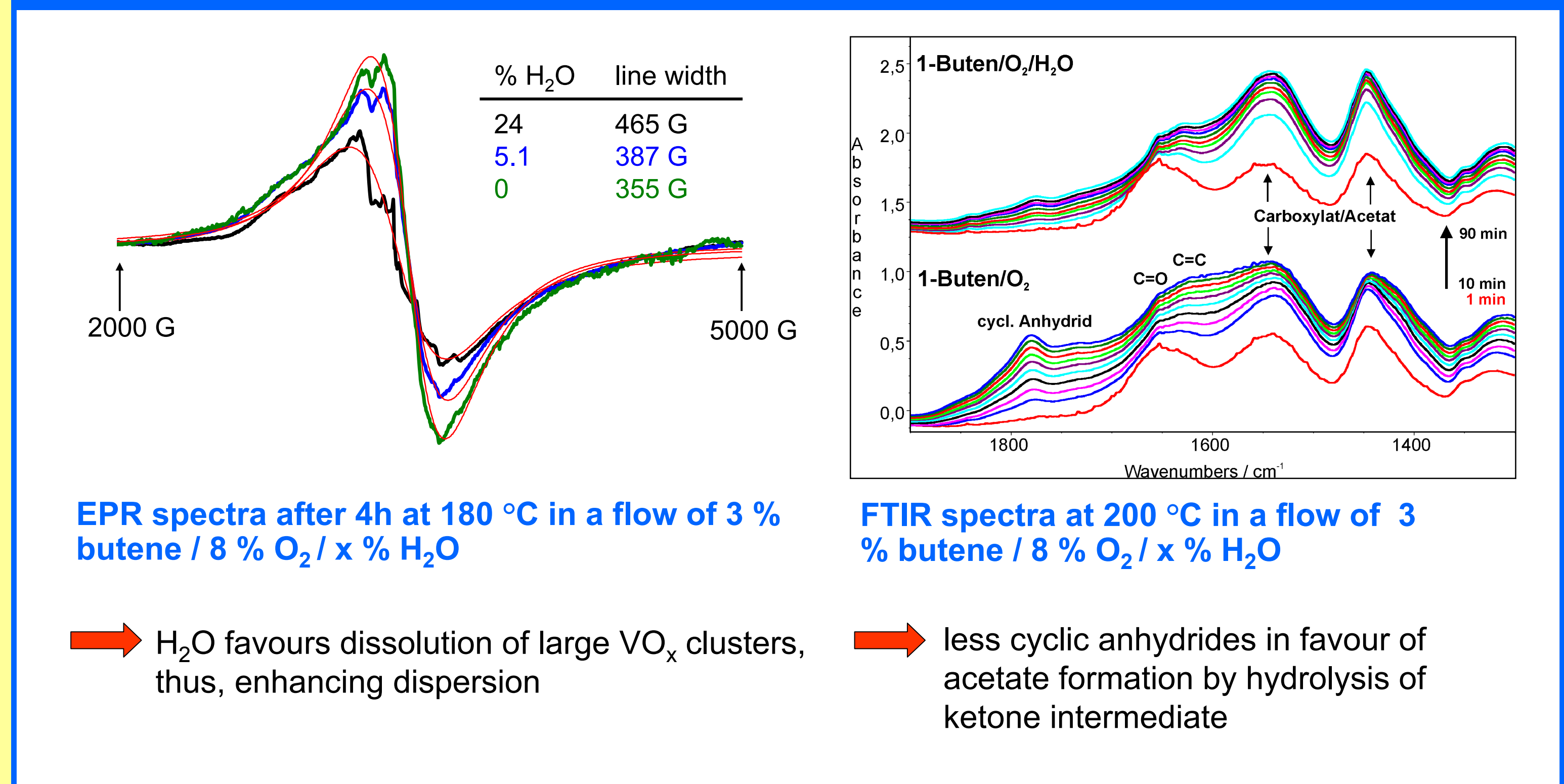
Feed: 1.9 % 1-butene, 9.1 % O<sub>2</sub>, 24.4 % H<sub>2</sub>O/N<sub>2</sub>, GHSV = 3730 h<sup>-1</sup>, p = 1 bar

- Sb doping rises activity and AA selectivity
- sulfate doping rises activity markedly
- non-redox support (Al<sub>2</sub>O<sub>3</sub>) poorly active
- increasing V content above 3.3 % leads to no further improvement

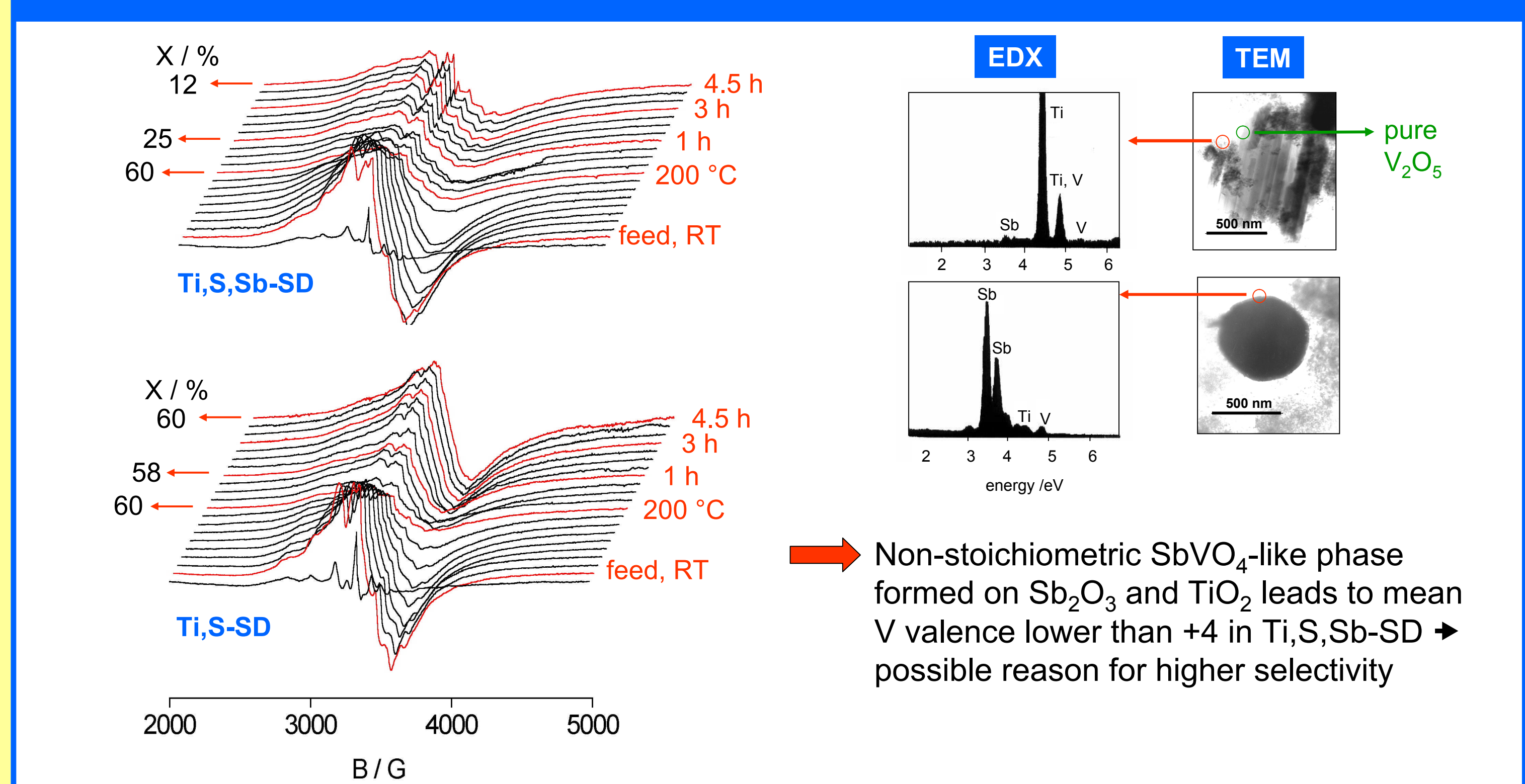
## Influence of support



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



## Influence of Sb doping



## Influence of sulfate doping

