

**Structure-reactivity relationships in supported VO_x/TiO₂ catalysts
for the oxyhydrative scission of 1-butene to acetic acid:
A comprehensive catalytic and in situ-spectroscopic study**

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Butene and butane are available as by-products of naphtha cracking applied for the production of ethene and propene. The effective use of these C₄ hydrocarbons could be realized by a new process based on the oxyhydrative scission of butene and butane to acetic acid [1]. At low reaction temperatures (ca. 200°C) and in the presence of water vapour n-butenes are selectively oxidised to acetic acid and/or acetaldehyde on titania supported vanadia catalysts. To make this process economical attractive, in particular with respect to n-butane conversion, knowledge about the reaction mechanism and specific function of the catalyst is necessary to improve the catalyst properties and its performance.

In situ-FTIR, -EPR, and UV-VIS spectroscopic methods were used to study the interaction of feed components (1-butene, O₂, H₂O) with VO_x/TiO₂ (3.9 - 9.0 wt.% V) and VO_x/SbO_y/TiO₂ (9.5 wt.% Sb) catalysts with different TiO₂ supports (sulfate-containing and sulfate-free anatase, rutile) under reaction conditions. The catalysts have been prepared by spray drying of an oxide mixture or impregnation followed by calcination in air at 400°C. Catalytic standard tests were performed at a total pressure of 7 bar in a fixed-bed plug-flow reactor at 180°C (feed 1.9 % 1-butene, 9.1 % O₂, 24.4 % H₂O/N₂).

Catalytic tests and in situ spectroscopic investigations demonstrated in good agreement that only catalysts with sulfate-containing anatase support work with good performance giving high acetic acid (AA) selectivities of about 70%. As shown by UV-VIS and FTIR the specific function of sulfate in the anatase support consists mainly in connecting the VO_x species to the support in a specific manner. In this way the active VO_x species will be stabilised at the catalyst surface leading to optimized redox properties of the catalysts. The admixture of Sb influences the surface acidity and the redox behaviour of the catalysts. Probably the formation of a non-stoichiometric amorphous Sb vanadate phase lowers the vanadium redox potential and causes a further improved AA selectivity. Even at room temperature an intensive interaction of butene with the catalysts proceeds indicated by a strong increase of the VO²⁺ signal intensity during EPR measurement and the appearance of adsorbed oxidized products (ketone, enolate) detected by FTIR. During reaction at 200°C a continuous increase of the VO²⁺ signal intensity is observed, whereas for the Sb-containing catalyst the formation of V³⁺ seems to be favoured. A rapid reaction accompanied by the formation of ketone, acetate and cyclic anhydride being a precursor for total oxidation has been observed by FTIR investigations. In the presence of water vapour the formation of anhydride is markedly suppressed in favour of acetate formation. This indicates the importance of water admixture for getting high AA selectivity. Changes of the VO²⁺ EPR signal shape upon adding water vapour suggest an increasing dispersion of active V sites.