



# On the mechanism of the catalytic oxidation of 1-butene to acetic acid in presence of water

W. Suprun<sup>a)</sup>, T. Machold<sup>a)</sup>, B. Kubias<sup>b)</sup>, H.-J. Eberle<sup>c)</sup>, C. Rüdinger<sup>c)</sup>, H. Papp<sup>a)</sup>

<sup>a)</sup> Institut für Technische Chemie, Universität Leipzig, Linnestr. 3, D-04103 Leipzig

<sup>b)</sup> Fritz-Haber-Institut, Abt. Anorganische Chemie, Faradayweg 4-6, D-14195 Berlin

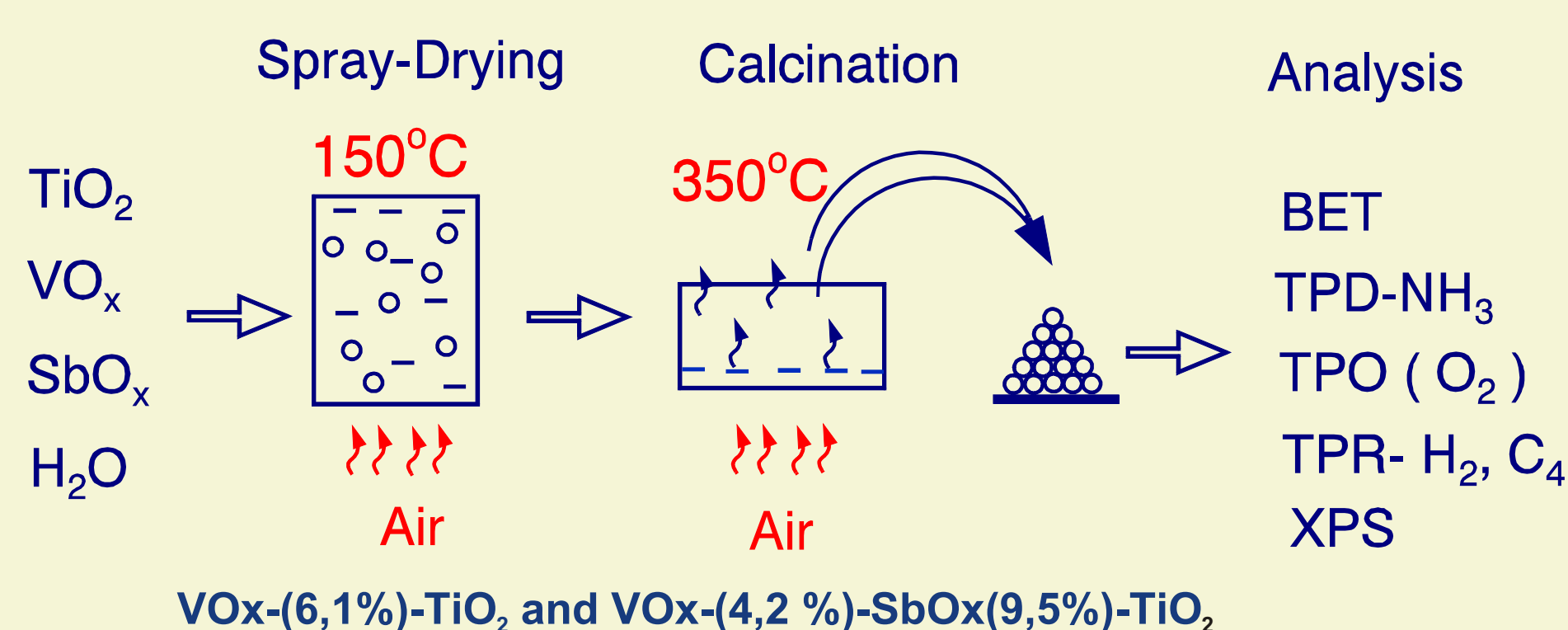
<sup>c)</sup> Consortium für elektrochemische Industrie GmbH, Zielstattstr. 20, D-81379, München

## Introduction

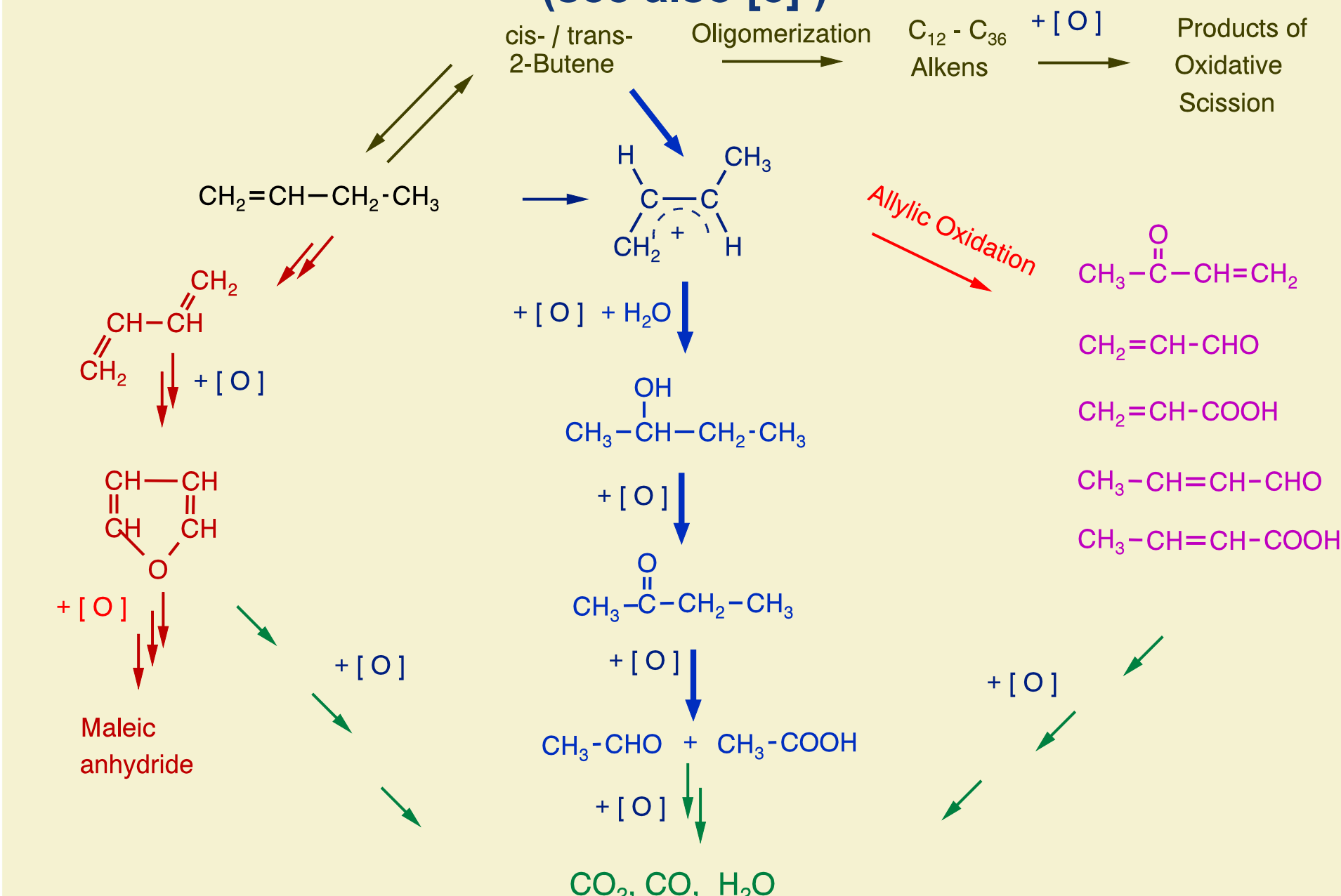
Acetic acid (AcOH) on industrial scale is produced by carbonylation of methanol [1]. Gas phase oxidation of n-butenes on VOx catalyst is also a potential route for the production of AcOH on smaller industrial scale of ~ 100 t/a. The mechanism of butene oxidation to AcOH is still a matter of discussion. Seyama et al. proposed an oxyhydrative scission mechanism involving water as a reactant [3]. In contrast, Kaneko et al. suggested a reaction mechanism without the participation of water [4]. This investigation was aimed at the elucidation of the reaction pathway for oxidation of 1-butene by transient isotopic method and steady state conditions.

## Experimental

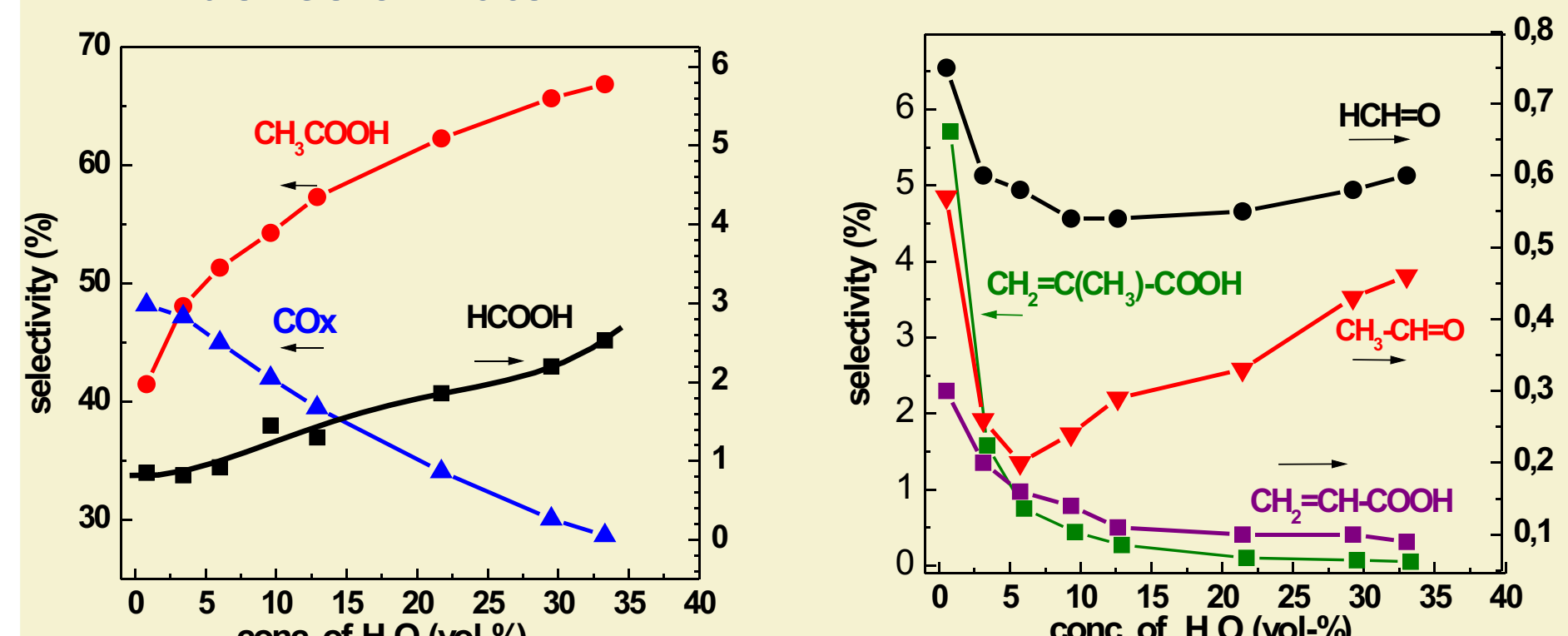
### Catalyst preparation [ 2 ]



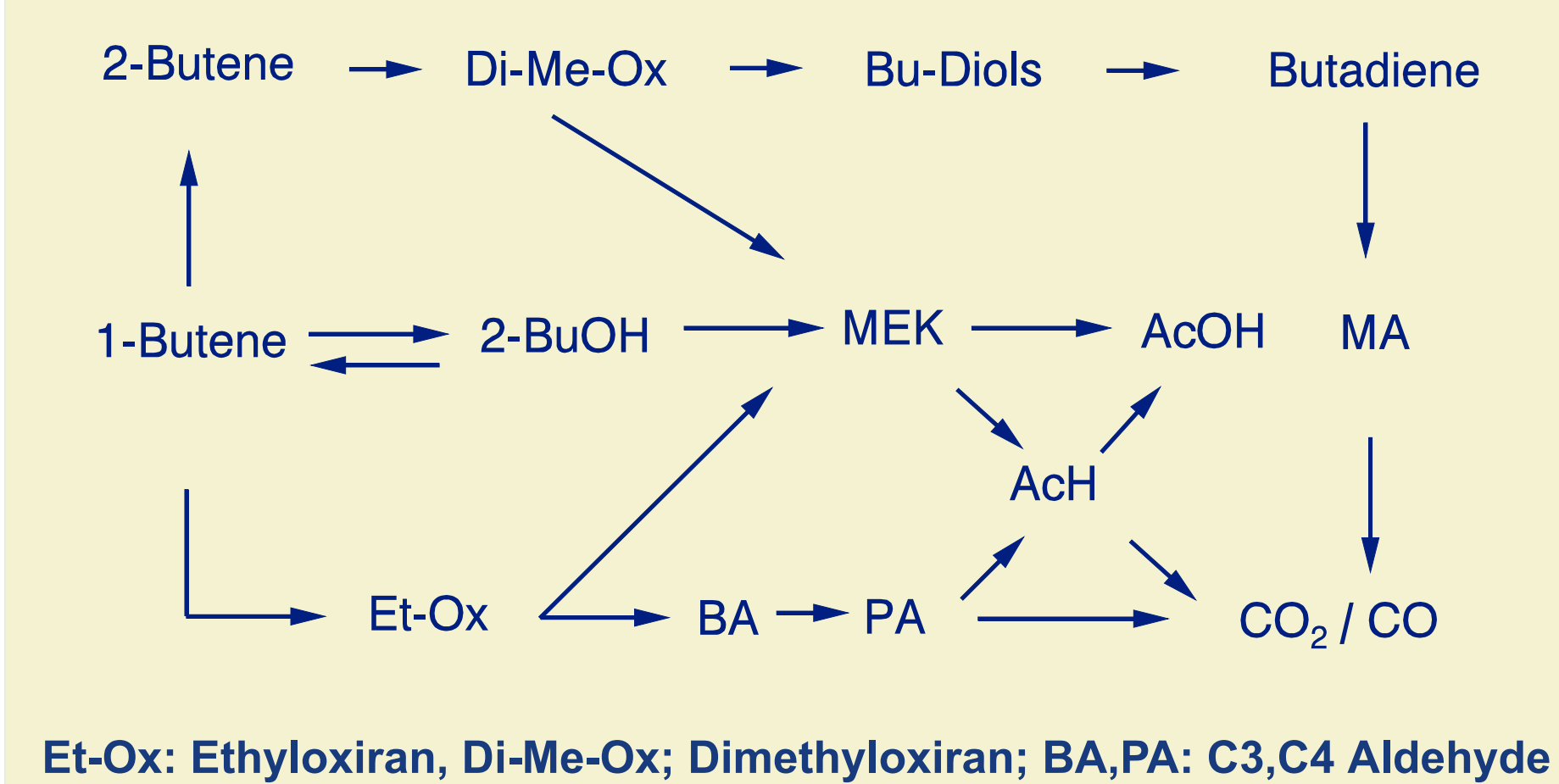
### Reaction network of n-butene oxidation on VOx catalysts (see also [5])



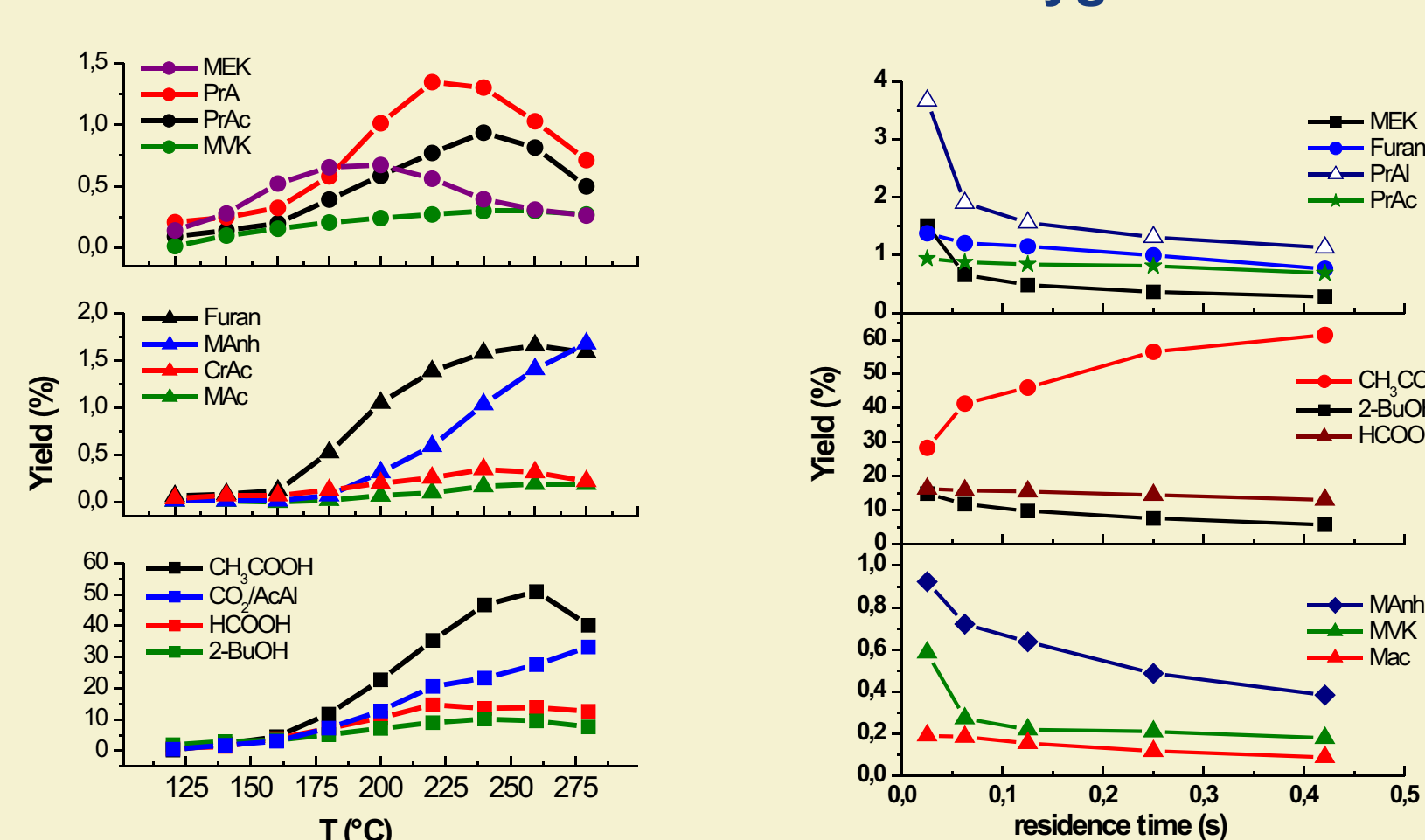
### Influence of water



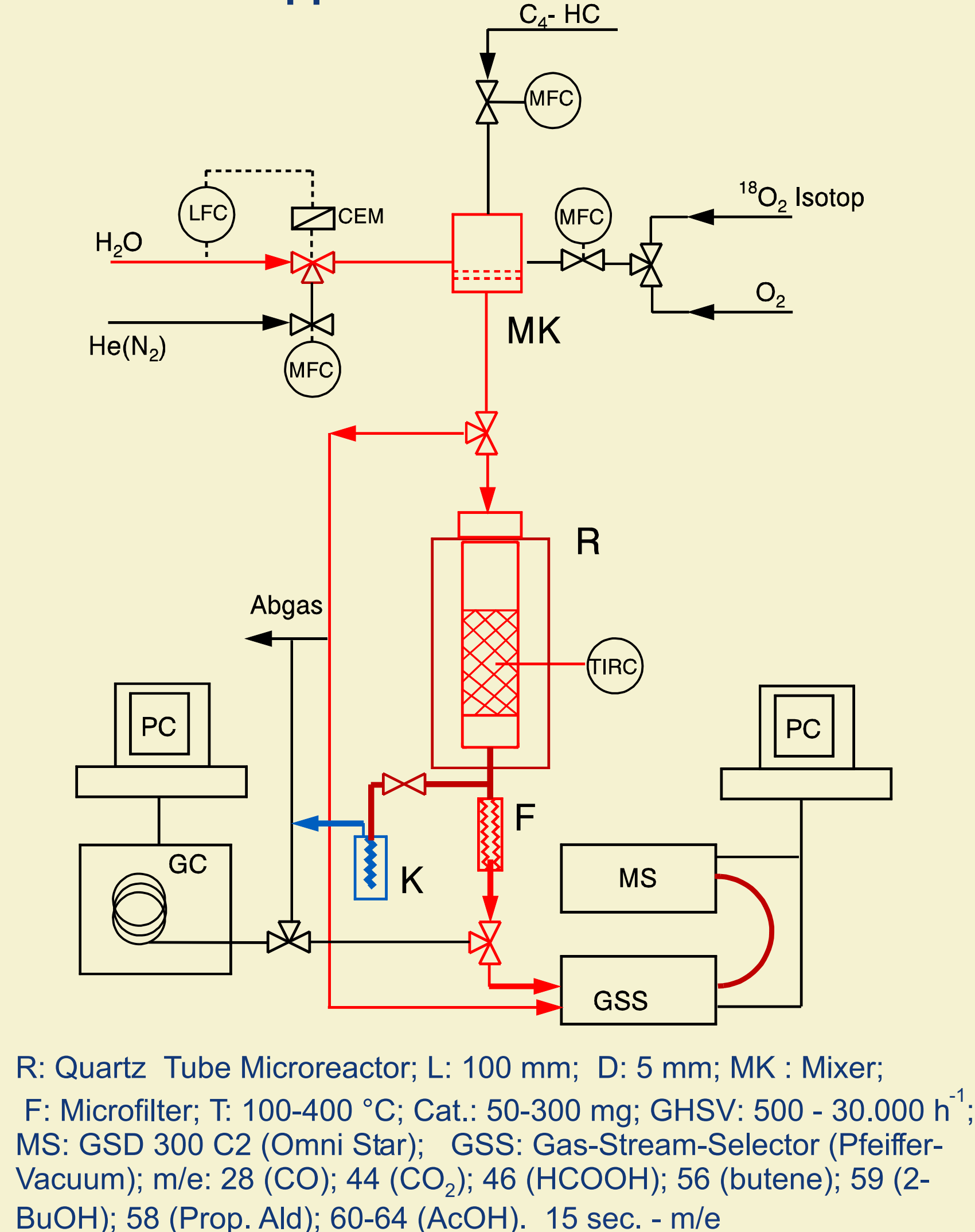
### Possible reaction network of the formation of AcOH



### Formation of acetic acid and other oxygenates

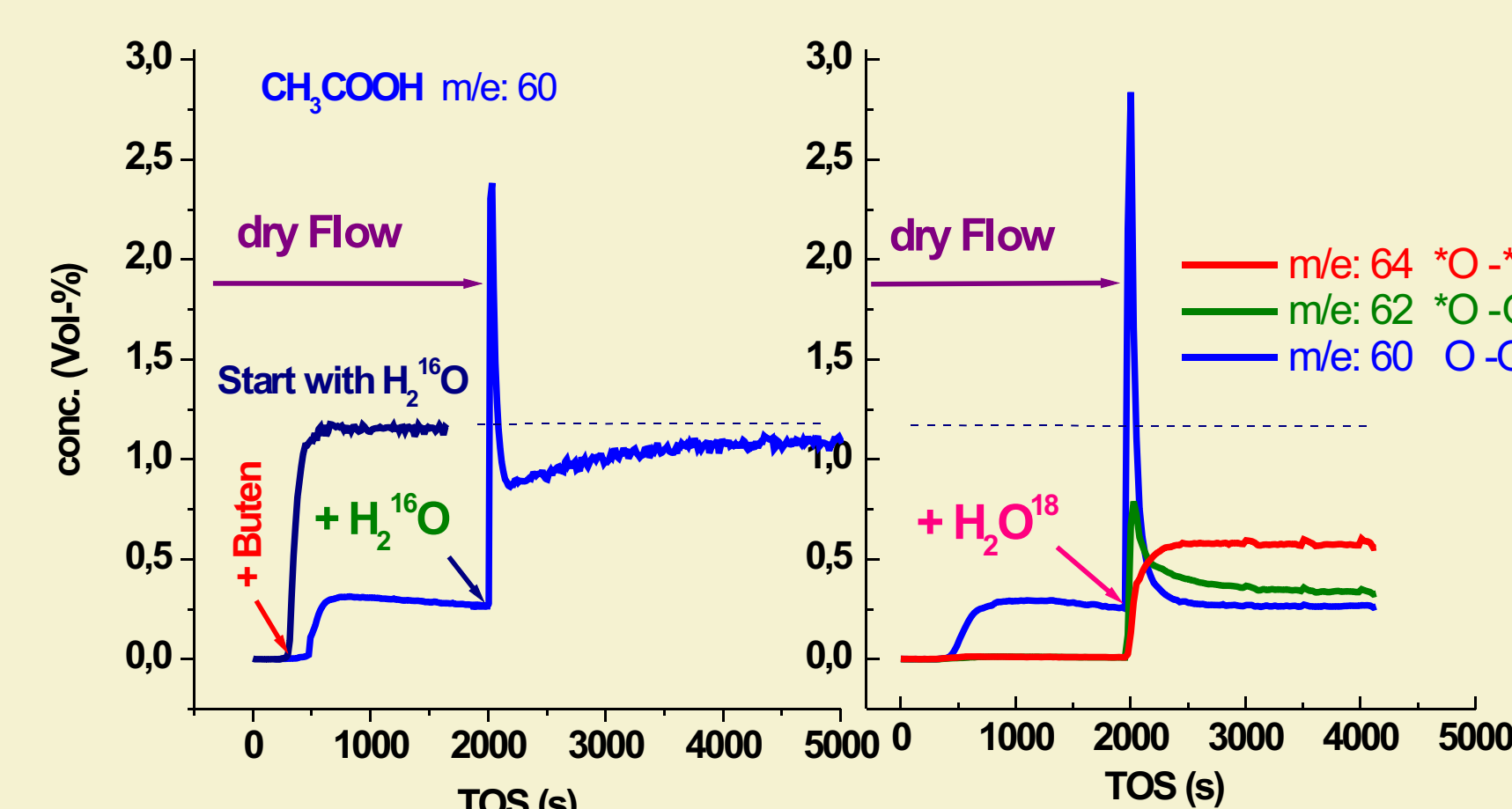


### SSITKA-Apparatus

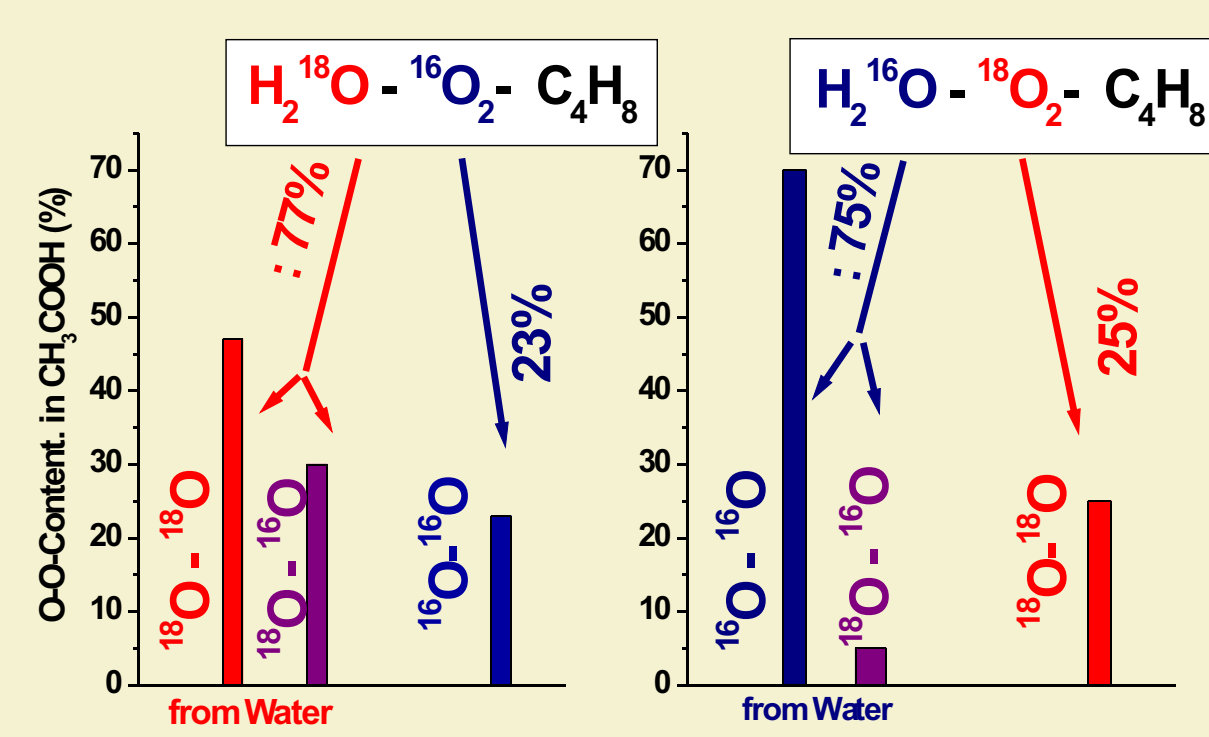


### Formation of AcOH during the catalytic oxidation of 1-butene in dry gas flow and in presence of H<sub>2</sub>O

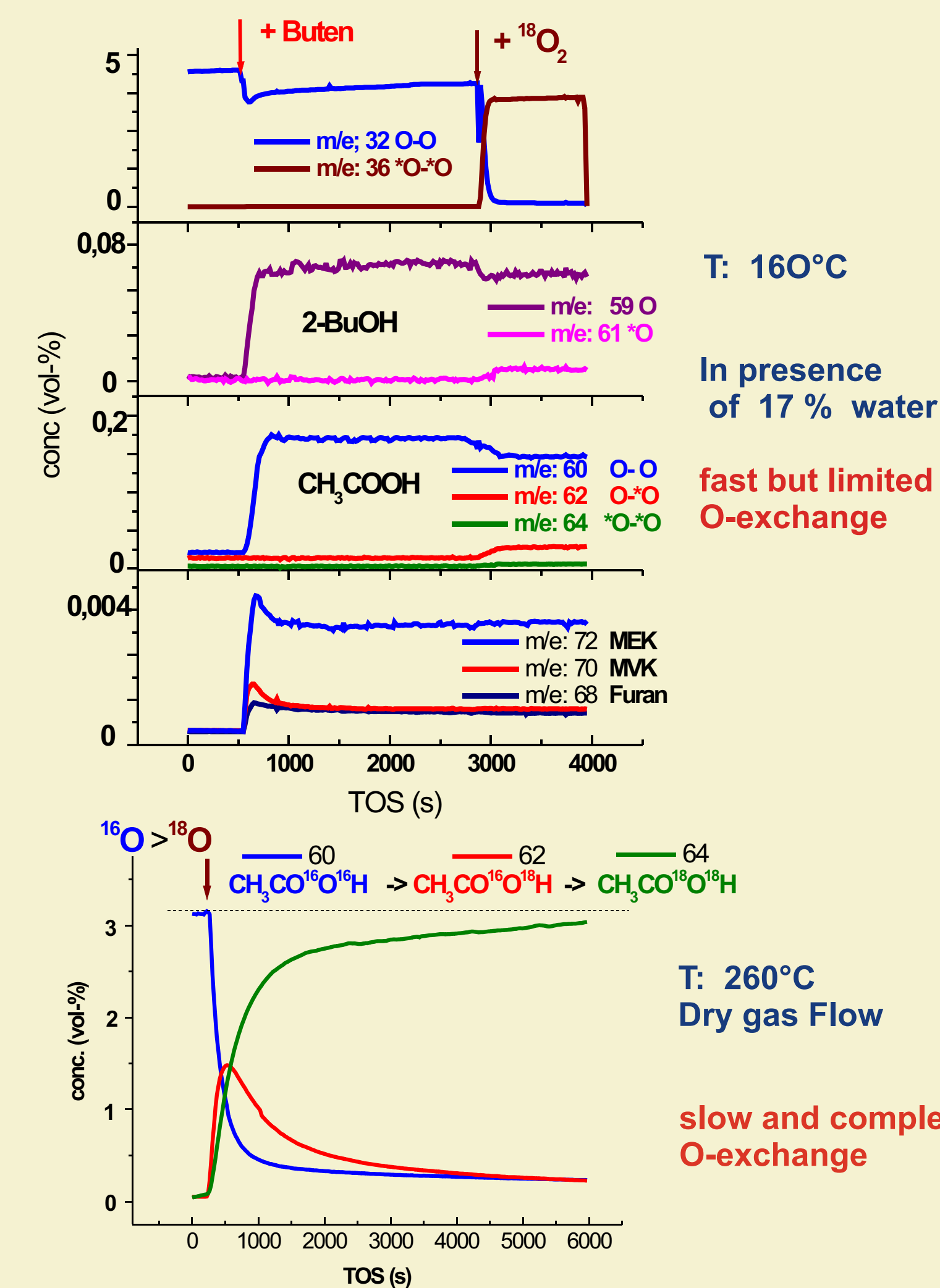
T: 220°C; O<sub>2</sub>: 5%; H<sub>2</sub>O: 17 vol-%; GHSV: 17.000 h<sup>-1</sup>



O-isotope distribution in CH<sub>3</sub>COOH during oxidation of 1-butene with oxygen <sup>18</sup>O (<sup>16</sup>O) on VOx-TiO<sub>2</sub> and in presence of water



### Formation of isotopic exchanged oxygenates after switching from <sup>16</sup>O<sub>2</sub> to <sup>18</sup>O<sub>2</sub>



## Results

### Steady state and transient isotopic experiments

- Formation of > 30 products including C<sub>1</sub>-C<sub>5</sub> carboxylic acids and anhydrides with AcOH as main product at low temperatures (<250°C)
- Influence of added H<sub>2</sub>O at low temperatures: promoted formation of AcOH and HCOOH, H<sub>2</sub>O suppressed allylic oxidation and total oxidation; increase of temperature (>300°C): MA is predominantly formed
- S<sub>AcOH</sub> in MEK oxidation higher than in 2-BuOH oxidation: parallel pathways from butene to AcOH exist
- Dioxolane and dioxan derivatives (formation by dimerisation of the potential intermediate products ethyloxirane and dimethyloxirane) were identified as products
- Transient oxidation of 1-butene with <sup>16</sup>O<sub>2</sub>/<sup>18</sup>O<sub>2</sub> switching in presence of H<sub>2</sub>O: fast but limited isotopic exchange in absence of H<sub>2</sub>O: slow and complete isotopic exchange

## Conclusions

- SSITKA experiments: water is involved in the formation of BuOH and AcOH.
- An oxyhydration step takes place in butene oxidation at low Temperatures.
- Steady state experiments: two reaction paths from butene to MEK exist:
  - 1) via 2-BuOH formed by hydration of n-butenes
  - 2) via dimethyl- and ethyloxiranes formed by electrophilic attack of oxygen species on the double bond in butene molecules
- AcOH is formed by oxidative scission of MEK
- During butene oxidation to AcOH both, the mechanisms of Seyama [3] and Kaneko [4] operate. Their individual contributions to the formation of AcOH remain a subject of further investigations.

## References

1. Chem Systems „Acetic Acid / Anhydride 97/98-1“, Jan. 1999
2. Ch. Rüdinger, H.-J. Eberle, N. Zeitler, DE 19649426, 1996
3. T. Seyama, K. Nita, T. Maehara, N. Yamazone, Y. Takita, J. Catal. 49 (1967) 163
4. K. Kaneko, T. Hoshio, S. Wada, Bull. Jap. Petr. Ins. 16 (1974) 24
5. G. Centi, F. Cavani, F. Trifiro, Selective Oxidation by Heterogeneous Catalysis, Kluwer, 2001, 449

## Acknowledgment

This work was supported by the German Federal Ministry of Education and Research (grant no. 03C0323C).