## PAUL SCHERRER INSTITUT





## Radical Chemistry in Oxidative Dehydrogenation of Propane over **Boron Nitride**

Zihao Zhang<sup>1</sup>, Ivan Surin<sup>2</sup>, Patrick Hemberger<sup>1</sup>, Andras Bodi<sup>1</sup>, Javier Pérez-Ramírez<sup>2</sup>

<sup>1</sup> Paul Scherrer Institute, 5232 Villigen, Switzerland

<sup>2</sup> Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland

Motivation

Oxidative dehydrogenation of propane (ODHP)

V/SiO<sub>2</sub>

## Experimental approach

*Operando* synchrotron photoelectron photoion coincidence (PEPICO) spectroscopy at Swiss Light Source of PSI





- (1) Main byproducts are  $CO_x$  (CO,  $CO_2$ ) on V-based catalysts, but are ethylene and methane in ODHP.
- (2) Peculiar kinetic features on boron nitride (BN) implies the existence of gas-phase radical reactions.

**Issue**: Radical chemistry in OHDP over BN is not well identified experimentally.

RT bckg RT bckg MB Field-free drift Photoionization DC extraction mass spectra  $DPI \rightarrow KER$ mbar 10<sup>-4</sup> mbar VMI focusing Isomer-selective catalysts Skimmer Pump identification of short-lived reactive microreactor  $C_{3}H_{8} + O_{2}$ intermediates Direction selection drift threshold e Field-free Photoion masshot e selected threshold photoelectron spectrum (ms-TPES) inverted image raw image **Electron detector** 

Results

Mass spectra of ODHP on BN and V/SiO<sub>2</sub> catalysts at (a) 9 eV and (b) 10 eV at 650 °C

(c) ms-TPES of m/z 41







- Gas-phase radicals were only observed for ODHP on BN, including methyl and allyl radicals at 650 °C, as well as 1propyl radical at higher reaction temperature.
- Radical chemistry on BN contributes to the formation of oxygenates (ketenes and ) and value-added  $C_4$ .

## Acknowledgement

PSI CROSS project funding initiative and National Centre of Competence in Research funded by the Swiss National Science Foundation are gratefully acknowledged.