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SELECTIVE ALKANE ACTIVATION BY CATALYTIC OXYHALOGENATION

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Project Summary: Catalytic oxyhalogenation of methane into halomethanes (CH_3X and CH_2X_2; X = Cl, Br) and of higher alkanes (ethane, propane, butane) directly into olefins constitute an attractive technology with the potential to develop processes for the on-site valorization of natural gas into chemicals and liquid fuels. To achieve this goal, catalysts that allow to selectively activate the alkane are highly sought after. Herein, a holistic approach that combines kinetic analyses with mechanistic understanding is used to design optimal catalysts for the oxyhalogenation of C_1-C_4 alkanes. In particular, *operando* prompt gamma activation analysis and photoelectron photoinon coincidence spectroscopy were utilized, in combination with theoretical calculations, to uncover surface properties and radical-based routes, respectively, during reaction conditions. This approach revealed that methane activation in oxychlorination has comparable contributions from surface and gas-phase pathways, while in oxybromination gas-phase radical chemistry is predominant, which is preferred to attain a high selectivity to halomethanes. On the other hand, the oxychlorination of higher alkanes was found to proceed exclusively over the catalyst surface, which was pivotal to achieve selective (≥ 95%) olefin formation. Accordingly, several catalyst families were discovered, including supported metal nanoparticles for methane oxyhalogenation as well as metal carbides, phosphates, and oxychlorides for olefins production. Finally, we demonstrated that in ethane and propane oxybromination, alkane activation *via* radical chemistry is dominant, causing limited (≤ 60%) olefin selectivity. This understanding enabled us to develop a novel catalytic process for the production of ethylene and propylene, surpassing any existing olefin generation technology.

CV. G. Zichittella obtained his M.Sc. in Chemical and Bioengineering at ETH Zurich in 2015. During this time, he conducted his master thesis in the group of Prof. J. Pérez-Ramírez, where he then continued with his doctoral studies.