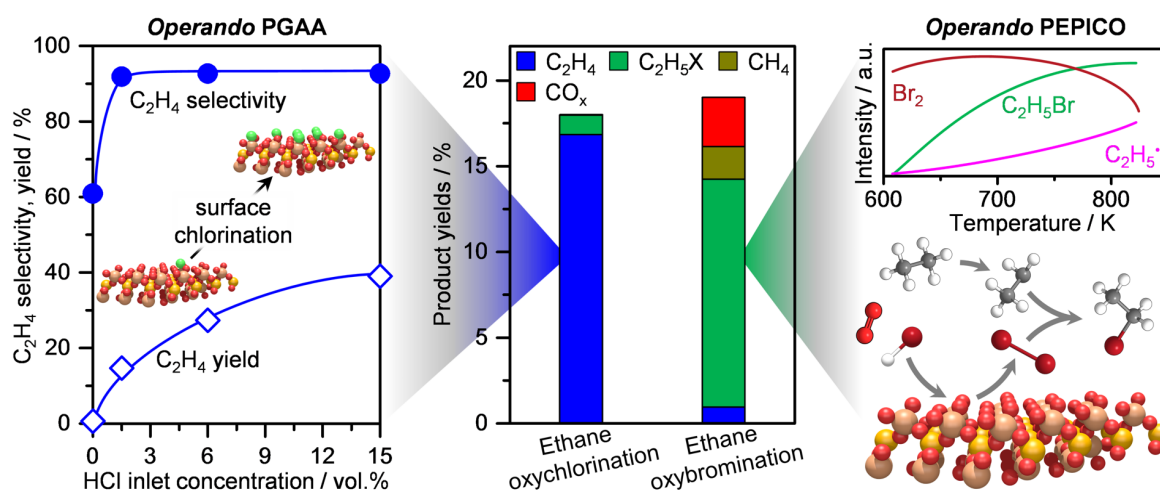


## Mechanistic origin of the halogen-dependent selectivity switch in catalyzed alkane oxyhalogenation

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Catalytic alkane oxyhalogenation, comprising the reaction of an alkane with O<sub>2</sub> and hydrogen halide (HX, X = Cl or HBr) has been recently demonstrated as a promising strategy for the functionalization of natural gas into light olefins and/or alkyl halides, both key building blocks for the manufacture of chemicals, polymers, and pharmaceuticals. Although several systems were shown to be efficient catalysts (e.g. iron phosphate, europium oxyhalide, titanium dioxide),<sup>1,2</sup> there is still no clear understanding on the mechanism of this reaction. In this study, we couple *operando* prompt gamma activation analysis (PGAA) to determine the amount of surface halogen species on iron phosphate (FePO<sub>4</sub>), as well as *operando* photoelectron photoion coincidence (PEPICO) spectroscopy to quantify the presence of radical species under reaction conditions (Figure 1). This is combined with steady-state kinetic tests and Density Functional Theory calculations that rationalized the observed favored olefin production (selectivity ≥ 95%) in oxychlorination and the preferred generation of alkyl bromides (selectivity ≤ 95%) in oxybromination (Figure 1). In particular, although both reactions undergo alkyl halide generation and consecutive dehydrohalogenation steps, it was found that alkane activation occurs primarily on the catalyst surface in oxychlorination, while it follows a radical-chain mechanism in the gas phase with the Br<sub>2</sub> produced *in situ* during oxybromination, originating the observed selectivity differences (Figure 1).



**Figure 1** Unraveling the reaction pathways involved in ethane oxychlorination (left) and oxybromination (right) over FePO<sub>4</sub> leading to the observed selectivity patterns (middle).

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