Olefins from natural gas via oxychlorination catalysis

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Ethane and propane, found in copious amounts in natural gas, comprise promising feedstocks to produce ethylene and propylene, the platform molecules for the manufacture of virtually all polymers, pharmaceuticals, and chemicals. However, the current routes to generate these pivotal olefins are (*i*) highly capital- and energy-intensive, and more alarmingly, (*ii*) unable to close the growing gap between their demand and availability.[1] Consequently, new versatile catalytic processes that can handle complex emerging feedstocks, such as shale gas, tight gas, and coalbed methane, are highly demanded. Oxyhalogenation, comprising the reaction of an alkane with a hydrogen halide (HX, X = Cl, Br) and O_2, has proven a highly effective and versatile route for alkane functionalization.[2] By investigating different families of materials, we discovered that europium oxychloride (EuOCl) provides single-pass yields to ethylene (90%) and propylene (40%) surpassing any previously reported route (**Figure 1**). Its outstanding performance was rationalized by (*i*) its balanced redox properties that enables the functionalization of the alkane while avoiding combustion, and (*ii*) its unpaired ability to dehydrochlorinate the formed alkyl chloride to the olefin, permitting the recycling of the halogen. This concept was extrapolated to mixtures of methane, ethane, and propane, achieving comparable olefin yields at >95% selectivity, respectively, demonstrating the uniqueness of the EuOCl catalyst for the selective functionalization of multiple hydrocarbon substrates at the same time without the need of highly energy intensive cryogenic pre-separation methods.

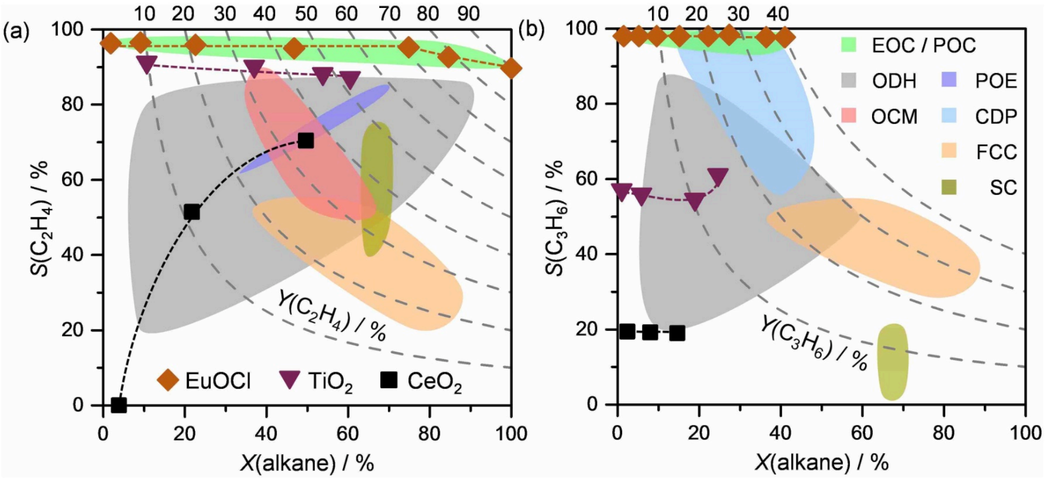

Figure 1 Alkene selectivity *versus* alkane conversion in the oxychlorination of (a) ethane (EOC) and (b) propane (POC) over EuOCl, TiO_2, and CeO_2. Dashed gray lines indicate the olefin yield, colored areas denote the single-pass molar alkane conversion and olefin selectivity achievable in EOC, POC, the oxidative dehydrogenation of ethane and propane (ODH), partial oxidation of ethane (POE), oxidative coupling of methane (OCM), catalytic dehydrogenation of propane (CDP), fluid catalytic cracking (FCC), and steam cracking (SC) of ethane and naphtha.

[1] J. J. H. B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, B. M. Weckhuysen, *Chem. Rev.* **2014**, 114, 10613.
[2] G. Zichittella, V. Paunović, A. P. Amrute, J. Pérez-Ramírez, *ACS Catal.* **2017**, 7, 1805.