Mechanism of ethylene oxychlorination on RuO_2 and CeO_2

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The manufacture of polyvinyl chloride (PVC) relies on the production of vinyl chloride (VCM) *via* a two-step process comprising ethylene oxychlorination to ethylene dichloride (EDC) on intrinsically unstable cupric chloride catalysts and a subsequent energy-intensive thermal cracking. Recently, we demonstrated that certain oxides or oxychlorides (*e.g.*, CeO_2) could serve as stable bifunctional catalysts, performing the two reactions in a single step and attaining VCM in up to 25% yield.[1,2] To gain deeper understanding of the oxychlorination mechanism, we investigate the complex reaction network by density functional theory (DFT), kinetic testing, and advanced characterization. In a first step, decoupling the complexity of the reaction network and CeO_2, DFT calculations were conducted on the simpler RuO_2, revealing the thermodynamic and kinetic control of oxidation and chlorination processes, respectively. Furthermore, the degree of chlorine coverage emerged as a key factor governing the selectivity, as it confines or destabilizes intermediates and determines the ability of the surface to abstract H atoms. This enabled simplification of the reaction network (**Figure 1**) for its investigation on a CeO_2 {111} surface in a second step. Preliminary results suggest that an ideal CeO_2 surface is unable to catalyze oxychlorination as the barriers for all important chlorination and dehydrogenation steps are 1.7 eV and higher. The introduction of defects, *i.e.,* by replacing a surface O by a Cl atom which can react and form a vacancy, leads to at least 0.5 eV decreased barriers for most chlorination reactions. Inspired by these results, we are developing a microkinetic model and experimentally assessing the impact of vacancies formed by controlled reduction of CeO_2 on its oxychlorination performance. Previously, acidity was shown to be strongly related to VCM selectivity,[1,2] but the exact nature of the sites remained unknown. DFT indicates that ceria acts as a Brønsted and Lewis acid/base pair, encouraging the investigation of the acid sites by solid-state NMR spectroscopy after adsorption of the probe molecule trimethylphospine. The combination of these results will reveal the detailed mechanism of ethylene oxychlorination on oxide-based catalysts and guide the development of more selective VCM catalysts.

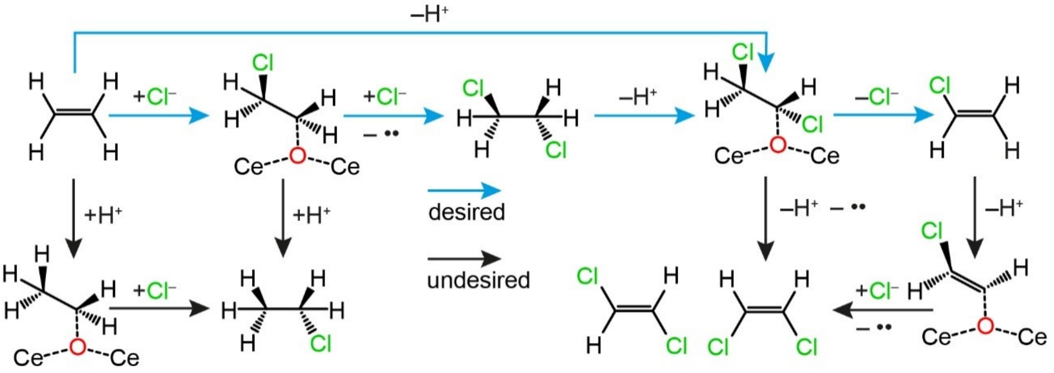

Figure 1 Simplified reaction network of ethylene oxychlorination, excluding oxidation steps which can start at any node.

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[2] M. Scharfe, P.A. Lira-Parada, A. P. Amrute, S. Mitchell, J. Pérez-Ramírez, *J. Catal.* **2016**, 344, 524.