

## **Oxidative dehydrogenation of ethane over supported chloride catalyst**

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The continuously increasing demand of ethylene and propylene as starting materials for petrochemicals and fine chemicals, has spurred substantial interest in the development of alternative routes to fluid catalytic cracking and naphtha cracking. Catalytic oxidative dehydrogenation (OHD) of alkanes and catalytic dehydrogenation (HD) combined with selective hydrogen combustion (SHC) present possible alternative. However, both approaches are still commercially unattractive because efficient catalysts have not been developed.

Here we report on the catalytic performance of supported chloride and oxychloride materials for oxidative dehydrogenation of ethane to ethylene. These catalysts show the best performance when the active phase is present as a layer of molten salt (chloride or oxychloride) on top of a chloride precursor. Two series of catalysts are compared, materials based on alkali metals and materials containing  $\text{AlCl}_3$  as one of the components. The materials show superior catalytic properties when present as melt, as compared to a solid catalyst. This suggests that the defect chemistry present in the solid materials is responsible for the oxidation to carbon oxides. A systematic correlation between ethylene selectivity and melting point of the eutectic mixture has been traced which allows tailoring catalyst design. Ethene yields of up to 80 % were obtained with the best catalysts.

A new radical-based mechanism was proposed wherein the catalytically active species have been identified to be hypochloride  $\text{OCl}^\cdot$  ions, formed by oxidizing  $\text{Cl}^-$  ions with  $\text{O}_2$  dissolved in the melt. The effectiveness of  $\text{OCl}^\cdot$  relies on its disproportionation to  $\text{O}^\cdot + \text{Cl}^- \leftrightarrow \text{O}^- + \text{Cl}^\cdot$ , whereby the radical species activate the ethane molecule by abstracting a hydrogen atom. Potential and limitations of this route of alkane activation will be discussed.