

# Interaction of HCl with a CeO<sub>2</sub>(111) Layer Supported on Ru(0001): A Theory-and-Experiment Combined Study

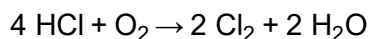
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The Deacon reaction is an environmentally friendly method to recover Cl<sub>2</sub> from HCl, an inevitable byproduct of several large-scale industrial processes such as polyurethane and polycarbonate production. In the Deacon process gaseous HCl is catalytically oxidized by O<sub>2</sub> to form water and the desired product Cl<sub>2</sub>:



Cerium(IV)oxide CeO<sub>2</sub> is considered as a promising alternative catalyst to the commercialized RuO<sub>2</sub>-rutile-TiO<sub>2</sub> catalyst developed by Sumitomo Chemical [1]. In this work [2], ultrathin crystalline CeO<sub>2</sub>(111) films were grown on Ru(0001) as model catalysts in order to study the interaction of HCl on a ceria surface as a first step in the Deacon reaction by a combined theoretical and experimental approach.

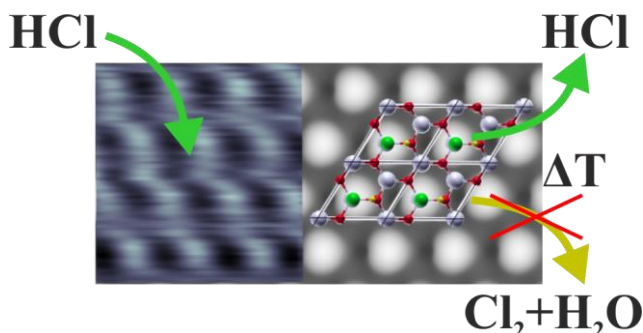


Figure 1: Atomic resolved STM image of the CeO<sub>2</sub>(111) ( $\sqrt{3} \times \sqrt{3}$ )R30° structure after exposing the CeO<sub>2</sub>(111) surface to 5 L of HCl at 300 K (left) in comparison with DFT-simulations of empty-state STM images (0-1.8 eV) (right). Superimposed is the calculated structure where H and Cl species and the outermost O and Ce ions are depicted as yellow, green, red and grey spheres respectively.

In this contribution, it is shown that the adsorption of HCl on CeO<sub>2</sub>(111) proceeds dissociatively in an acid-base type reaction with an adsorption energy of 1.15 eV. The hydrogen binds to a surface O site, while Cl resides in an atop position at a neighboring surface Ce site. HCl adsorption leads to the formation of an ordered overlayer structure: CeO<sub>2</sub>(111)-( $\sqrt{3} \times \sqrt{3}$ )R30°-H+Cl (LEED). The formation of such an ordered structure even at room temperature, indicates high mobility of Cl on CeO<sub>2</sub>(111) that is corroborated by a low activation energy for Cl diffusion of ~0.6 eV. Besides bonding of Cl and H to surface Ce and O atoms, respectively, an additional acid-base stabilization of H<sup>+</sup> and Cl<sup>-</sup> of ~0.4 eV is encountered. Upon heating the sample to 700 K

(TDS), only HCl (neither water nor H<sub>2</sub>) desorbs from the CeO<sub>2</sub>(111)-( $\sqrt{3} \times \sqrt{3}$ )R30°-H+Cl surface. This behavior is reconciled with the calculated minimum energy paths (DFT+U) for the adsorption and desorption process of HCl on the CeO<sub>2</sub>(111) surface, clearly evidencing that Cl-Cl association followed by Cl<sub>2</sub> desorption is less favorable than H-Cl recombination and desorption. From the findings of this study, we conclude that the stoichiometric CeO<sub>2</sub>(111) surface should not be active in the Deacon process at typical reaction temperatures of 700 K.

## References:

- [1] Amol P. Amrute, Cecilia Mondelli, Maximilian Moser, Gerard Novell-Leruth, Núria López, Dirk Rosenthal, Ramzi Farra, Manfred E. Schuster, Detre Teschner, Timm Schmidt, Javier Pérez-Ramírez, J. Catal. 286, 287-297 (2012).
- [2] Christian Sack, Pablo Lustemberg, Volkmar Koller, M. Verónica Ganduglia-Pirovano, Herbert Over, J. Phys. Chem. C *submitted* (2018).