

Towards a Mechanistic Understanding of the Catalytic Destruction of Chlorinated C1 Hydrocarbons on La-based Oxides

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Introduction

Chlorinated hydrocarbons (CHCs) are known for their many negative effects, such as destruction of the ozone layer, acid rain, the greenhouse effect and toxicity to organisms. In the last decades, the application of CHCs in commercial products has been reduced strongly and nowadays, chlorinated waste is almost exclusively produced in industrial processes. The industrial waste streams mainly consist of chlorinated C1 and C2 molecules and are currently incinerated at high temperatures. In order to find alternatives for the costly process of incineration, new materials for the low temperature conversion of CHCs have been investigated. Basic oxides are known to convert CHCs in the process of destructive adsorption, which involves the exchange of oxygen from the solid with chlorine from the gas phase molecule. By adding an excess amount of steam to the CHCs, lattice oxygen can be regenerated, making the process catalytic.

In previous research, lanthanum oxide based materials were found to have the best combination of activity and surface regeneration for catalytic destruction of CHCs [1,2]. Our group has extensively studied the mechanism of destructive adsorption on La-based materials of CCl₄ to gain insight into the surface reactions. [3] The presence of more chlorine at the surface increases the strength of the Lewis acid site and as a result the destructive capacity of the material [4]. However, the mechanism for the destructive adsorption of other chlorinated C1, such as CHCl₃, CH₂Cl₂ and CH₃Cl, is still not fully understood. In this study, activity experiments using GC reactor effluent analysis were combined with in situ IR spectroscopy to determine the mechanism for the destructive adsorption of CHCl₃, CH₂Cl₂ and CH₃Cl [5]. In addition, the activity dependency on the reactant and on the catalytic material was investigated.

Materials and Methods

LaOCl was prepared by a precipitation process using LaCl₃·7H₂O as precursor. In situ IR spectra were measured using a Perkin Elmer 2000 spectrometer. The reactions were performed in a quartz IR static vacuum cell. LaOCl was pressed into self-supporting 2 cm² wafers and was activated in situ. IR spectra of the gas phase and the wafer were measured as the temperature was increased in steps of 50 °C.

The activity measurements for the destructive adsorption of CHCl₃, CH₂Cl₂ and CH₃Cl were performed in a tubular fixed bed quartz reactor. The catalyst bed consisted of 1.0 g of synthesized LaOCl or commercial La₂O₃. The reactant flow was 6 vol% of CHC in He. The reactor effluent was analyzed by a Siemens Maxum Edition 2 GC. Temperature programmed reactions were performed to determine the initial temperature of reaction for each of the reactants. Constant temperature experiments were performed to enable comparison of activity between the reactants and different La-based materials.

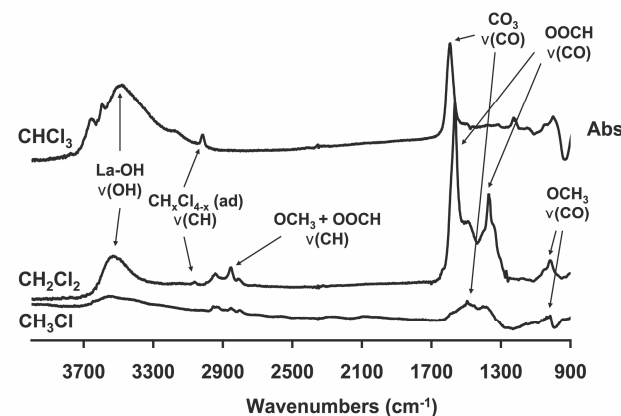


Figure 1. In situ IR spectra of surface species on LaOCl during the destructive adsorption of CHCl₃, CH₂Cl₂ and CH₃Cl at 250 °C.

Results and Discussion

The IR results show that the surface of the La-based materials is occupied by a mixture of carbonate, formate and methoxy groups during destructive adsorption of CHCl₃, CH₂Cl₂ and CH₃Cl (Fig. 1). The relative concentration of each of the surface intermediates is dependent on the Cl/H ratio of the reactant. The temperature and chlorination degree of the surface initiate decomposition of the surface species, leading to desorption of the products. The GC results show that the activity for the destructive adsorption of the H-containing chlorinated C1 decreases with decreasing chlorine content of the reactant. The polarization of the reactant molecule decreases with increasing H-content. As a result, the abstraction of a chlorine or hydrogen atom by the surface becomes less favorable and hence the activity decreases.

Significance

In this study, a general mechanism for the destructive adsorption of chlorinated C1 is proposed. This obtained insight is crucial to the design of new materials for the efficient conversion of CHC mixtures into non-hazardous products or re-usable chemicals.

References

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