

Influence of Steam on the Destructive Oxidation of *m*-Dichlorobenzene over V_2O_5/TiO_2 catalysts

Casey E Hetrick, Florian Patcas, and Michael D. Amiridis*
University of South Carolina, Columbia, SC 29208 (USA)
*amiridis@enr.sc.edu

Introduction

The destructive oxidation of chlorinated aromatics is the preferred method for controlling polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/PCDF) emissions. Supported vanadium oxide catalysts are used in this application commercially, particularly for incinerators, ore sintering, and coal combustion. [1]. Most research in this area has been conducted using chlorinated phenols and benzenes as model compounds due to their structural similarities with PCDD/PCDF.

The complete oxidation of *o*-, *m*-, and *p*-dichlorobenzenes, *o*- and *p*-chlorophenol, and 2,4,6-trichlorophenol over supported vanadium oxide catalysts has been systematically investigated in our group [2-5]. To clarify the phenomenology on the catalyst surface, combined kinetics and *in situ* infrared spectroscopic studies were performed. Surface species like phenolates, quinones, acetates, and maleates were detected on these systems. However, in the gas phase, only CO, CO₂, H₂O, and HCl were found to be present. In this study, we continue the investigation of intermediate formation in the oxidation of *m*-dichlorobenzene (m-DCB) on V_2O_5/TiO_2 both in the presence and absence of steam. In an attempt to investigate the reaction pathways, our work focused on the formation of surface and gas phase intermediates. Kinetic studies were also conducted with a 3.6 wt% V_2O_5/TiO_2 catalyst and different amounts of steam.

Materials and Methods

The 3.6 wt% V_2O_5/TiO_2 catalyst was prepared by incipient impregnation using ammonium metavanadate and titanium dioxide (Kimera-95, 79m²/g). *m*-Dichlorobenzene (Sigma Aldrich, 99+%) was used as purchased. On-line analysis was performed by GC-FID (HP5890 II, RTX-1 capillary column). The outlet gas flow was passed through a series of cooled traps for collection of reaction products. Their identification and analysis were performed on GC-MS (Finnigan, RTX-5 capillary column). A Nicolet 740 spectrometer and a homemade *in situ* flow cell were used for the FTIR investigation of the catalyst.

Results and Discussion

Total oxidation of dichlorobenzene (500 ppm, 10% O₂) was studied in a single-pass reactor. During analysis of the condensed products, we identified trace amounts of dichloro-hydroquinone, 2,3-dichloro-propaldehyde, maleic anhydride, and 2,3-dichloro-maleic anhydride.—The hydroquinone, maleic anhydrides, and aldehyde were also observed in the spectroscopic investigations.

An unexpected behavior of the catalytic system was observed during the addition of steam to the m-DCB feed. Figure 1 shows the light-off curves for the oxidation of m-DCB on V_2O_5/TiO_2 both in the presence and the absence of steam. When steam is added to the reaction mixture, three distinct regimes can be recognized in the conversion versus temperature curve. First, the oxidation activity increases as expected with temperature until 300°C (range A), but then decreases to a minimum at ca 350°C (range B) followed by a new increase of the conversion with the temperature above 350°C (range C). To our knowledge, no reports about this curious behavior have been published, with the exception of a very recent manuscript

regarding the oxidation of chlorobenzene with steam added at 200°C over a similar vanadia/titania catalyst [6].

The hysteresis behavior of the catalytic system and the distribution of the products in the temperature ranges A, B, and C were studied. The experimental results indicate that similar products are formed but in different ratios. The intermediate analysis also provided some evidence regarding the mechanism of oxidation. The presence of dichloro-maleic anhydride and dichlorobenzenes, for example, indicate that hydrogen abstraction may be occurring. Additionally, chlorinated hydroquinone and maleic anhydride were identified, which supports our previously proposed mechanism of oxy-dechlorination as the initial step.

Significance

This study contributes to the advancement of our basic knowledge regarding the total oxidation of chlorinated aromatics. Clarifying the reaction pathway and the role of the active sites, as well as the influence of steam on both intermediates formation and catalyst behavior, is crucial for understanding this process. At the same time, this is a basis for scientific development of a catalyst with improved performance characteristics for tailored applications.

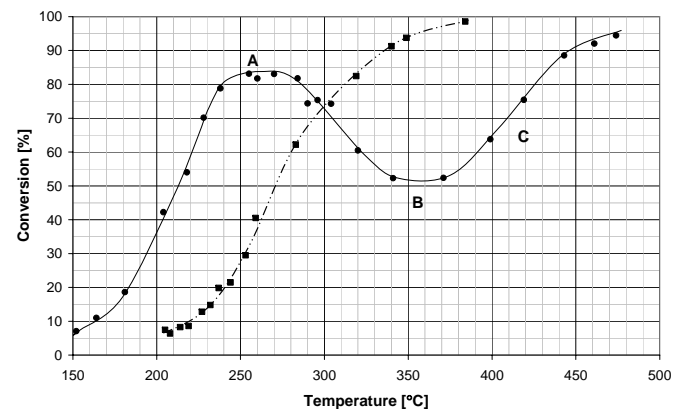


Figure 1: Light-off curves for *m*-dichlorobenzene oxidation with 5.0% (●) and without (■) steam (v/v).

References

1. Finocchio, E. Busca, G., and Notaro, M. *Appl. Catal. B: Env.* 62, 12 (2006).
2. Krishnamoorthy, S., Baker, J.P., and Amiridis, M.D. *Catal. Today* 40, 39 (1998)
3. Krishnamoorthy, S. and Amiridis, M.D. *Catal. Today* 51, 203 (1999).
4. Lomnicki, S., Lichtenberger, J., Xu, Z., Waters, M., Kosman, J., and Amiridis, M.D. *Appl. Catal. B: Env.* 46, 105 (2003).
5. Lichtenberger, J. and Amiridis, M.D. *J. Catal.* 223, 296 (2004)
6. Bertinchamps, F., Attianese, A., Mestdagh, M.M., and Gaigneaux, E.M. *Catal. Today* 112, 165 (2006)