



# Catalytic oxidation of 1,2-dichlorobenzene over $\text{CaCO}_3/\alpha\text{-Fe}_2\text{O}_3$ nanocomposite catalysts



Xiaodong Ma<sup>\*</sup>, Quan Sun, Xi Feng, Xuan He, Jie Guo, Hongwen Sun, Huiqin Cao

Key Laboratory of Environmental Pollution Process and Standard, Ministry of Education, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

## ARTICLE INFO

### Article history:

Received 17 July 2012

Received in revised form 6 October 2012

Accepted 8 October 2012

Available online 8 November 2012

### Keywords:

Chlorinated volatile organic compounds

1,2-Dichlorobenzene

Catalytic oxidation

$\text{CaCO}_3$

$\text{Fe}_2\text{O}_3$

## ABSTRACT

$\text{CaCO}_3/\alpha\text{-Fe}_2\text{O}_3$  nanocomposites were synthesized by one-pot method to develop a low-cost and environmentally friendly technology for the catalytic oxidation of 1,2-dichlorobenzene (*o*-DCB), a model of chlorinated volatile organic compounds. The nanocomposites were characterized by FAAS, XRD,  $\text{N}_2$  adsorption/desorption, TEM and XPS. Activity measurements were conducted in the range of 200–500 °C, in both the presence and absence of water. Among the tested catalysts, the nanocomposite with 9.5 mol% Ca showed the highest catalytic activity, which could be attributed to the promoting effect of  $\text{CaCO}_3$  on  $\alpha\text{-Fe}_2\text{O}_3$  with smaller crystallite size. Experimental results in the presence of water indicated that, due to the competitive adsorption of water on the active sites, there was a local minimum of catalytic activity at 350 °C. In situ FTIR experimental results revealed the presence of phenolate, catecholate, *o*-benzoquinone, carboxylate and anhydride type species on the surfaces of the catalysts during the oxidation of *o*-DCB. Spectral evidence discovered that the formate species were more prone to being formed on the surface of nanocomposite with 9.5 mol% Ca and then were further oxidized to CO, which directly lead to high activity of the catalyst. A mechanism involving dissociative adsorption of *o*-DCB on the surface of catalyst was proposed.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) from stationary sources have attracted widespread attention, due to their high toxicity, bioaccumulation and environmental persistence [1–4]. To effectively reduce Cl-VOCs emissions, stringent emission standards have been promulgated by many countries [5]. Catalytic oxidation of Cl-VOCs to  $\text{CO}_x$ ,  $\text{H}_2\text{O}$  and HCl has been thought as the most promising method for environmental protection due to its viable and economical advantages over the conventional methods such as thermal destruction and adsorption [6–10].

During the past decades, a number of catalytic processes for the total oxidation of Cl-VOCs have been reported. The previous research mainly focused on the development of two types of catalysts, namely the noble metal based catalysts and transition metal oxide based catalyst. The noble metal based catalysts such as Pt, Pd and Rh are more active at low temperature for total combustion of many Cl-VOCs. However, their relatively high cost and low stability toward the produced HCl and  $\text{Cl}_2$  have hindered their further development [8,11].

Alternatively, the transition oxide based catalysts, such as  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ , CuO,  $\text{Co}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ , NiO and  $\text{V}_2\text{O}_5$ , have been extensively studied as potential catalysts for Cl-VOCs decomposition [12–18]. However, excessive usage of some of these catalysts may enhance the risk of releasing toxic heavy metals into the environment. Recently, iron oxide-based catalysts have been paid more attention in the decomposition of Cl-VOCs due to their potential advantages such as environmental friend, low cost, high performance, and accessible raw materials [19,20].

Further researches have revealed that the Ca-doped iron oxide catalysts exhibited better catalytic activity for the decomposition of Cl-VOCs than single iron oxide [21–23]. While previous researches mainly focused on the catalytic activity of the Fe–Ca binary oxides, few work involved composite material. Recently, Matsui et al. reported that Fe–Ca–C composite catalysts exhibited high dechlorination activity for chlorocyclohexane [24]. However, systematic studies of the composition, activity and mechanism of Fe–Ca composite catalysts in the catalytic oxidation of Cl-VOCs are still lacking. Some important factors affecting catalytic activity have not been investigated in detail. For example, water, both an integral part of the flue gas emanating from the incinerators and a product of the total oxidation of the Cl-VOCs, has a significant influence on the catalytic performance, while the role of water in the catalytic system based on Fe–Ca composite is still ambiguous.

<sup>\*</sup> Corresponding author.

E-mail address: [maxd@nankai.edu.cn](mailto:maxd@nankai.edu.cn) (X. Ma).