

# Catalytic detoxification of C<sub>2</sub>-chlorohydrocarbons over iron-containing oxide and zeolite catalysts

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## Abstract

Catalytic hydrodechlorination is an effective and environmentally friendly alternative for the destruction of chlorine-containing organics. Since the byproducts are waste materials (HCl and Cl<sub>2</sub>), it is important to find and apply inexpensive or natural materials having catalytic activity in hydrodechlorination. A potential catalyst of this type, the calcined “red mud” originated from the alumina process, was studied in comparison with other iron-containing catalysts, such as single (Fe<sub>2</sub>O<sub>3</sub>) and mixed oxides (Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) and modified zeolite (Fe-ZSM5). The red mud is a dangerous waste formed in large amount, nevertheless, it contains catalytically active oxides. The hydrodechlorination reactions were carried out in a fixed-bed flow reactor in the temperature range of 200–400 °C using hydrogen as reducing agent. The structure of the catalysts was characterized by XRD, IR and adsorption methods. The metal and chlorine contents of the used samples were also determined. The efficiency of the reductive destruction of 1,2-dichloroethane (DCE), 1,1,2-trichloroethane (TRCE), 1,1,2,2-tetrachloroethane (TCE), trichloroethene (TRCEE) and tetrachloroethene (TCEE) over mixed oxide originating from red mud is comparable to that obtained for synthetic catalysts. The solids used are not only catalysts, but reactants as well in these reactions. Therefore, these processes could be considered as gas–solid reactions.

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## 1. Introduction

Halogenated- and more specifically chlorinated-volatile organic compounds (CVOCs) are widely used for various purposes commercially; however, there exists a well-known demand to decompose the waste of these chemicals to protect the environment. Due to their inertness and widespread industrial application, these compounds are main players in air and water pollution [1]. Chlorinated hydrocarbons are not only harmful directly for public health, but their long lifetime results in accumulation in the environment and the atmosphere contributing to the enhancement of global greenhouse effect and the depletion of the stratospheric ozone layer [2].

As dry cleaning and electronic industry solvents trichloroethene (TRCEE) and tetrachloroethene (TCEE) are

those organochlorinated compounds that are released into the atmosphere in the largest quantities. Both compounds are carcinogenic for humans and very harmful to the environment. However, their excellent physical and chemical properties make these materials difficult to replace in many applications, especially in dry cleaning. Thus, the abatement of chlorinated volatile organic compound emission is of high importance [3].

Today, the most commonly used process for eliminating CVOCs is thermal incineration requiring temperatures over 1000 °C to achieve complete combustion [4]. These high temperatures are costly because of corrosion and energy demand. Nitrogen oxides (NO<sub>x</sub>) are also formed in high quantities. Polychlorinated dioxins and dibenzofurans [5] might be formed as well.

Catalytic oxidation is carried out at relatively low temperatures (<600 °C) and, therefore, it is a highly energy efficient process compared to thermal incineration especially for low

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concentrations of CVOCs [6]. A proper catalytic process has a good potential for selective formation of harmless reaction products, and may result in the complete elimination of all halocarbons including toxic byproducts. However, the catalysts usually lose their activity rapidly due to the formation of HCl and Cl<sub>2</sub> [7].

Catalytic hydrodechlorination could be a safe alternative for the treatment of chlorinated organic wastes. This method has potential economic and environmental advantages over methods like thermal incineration and catalytic oxidation [8] because hydrodechlorination occurs at lower temperatures and it transforms the organochlorinated compounds into less harmful chlorine-free organic compounds, which can be safely recovered or burned [9]. The advantages include the ability to reuse the reaction products and minimal production of harmful byproducts.

Five main catalyst types have been reported for hydrodechlorination: supported noble metals [10,11], simple transition metal oxides, e.g., NiO/SiO<sub>2</sub> [12], mixtures of metal oxides such as Ni/Mg/Al oxide derived from hydrotalcite [13] or sulfided Ni/Mo-oxide [14] and modified zeolites [15–17]. Similarly to the oxidation catalysts mentioned earlier the high drawback is the poisoning of these materials by the HCl formed in the reaction, which means short lifetime and high operational costs.

Recently, development of catalysts based on waste materials is an issue of great interest because two environmental objectives could be fulfilled simultaneously: reusing the waste materials and saving the raw materials, such as catalyst precursors [18,19]. After proper pretreatment a waste material, the red mud can be considered as hydrodechlorination catalyst. Red mud is a byproduct in the Bayer process of alumina manufacturing, containing mainly oxides of iron, aluminum, titanium, silicon, calcium and sodium [20]. In Hungary, the annual red mud production is over three million tons in the last decades, and its average composition (Table 1) makes it an interesting base material. The environmental danger of red mud is originated from its high alkalinity, and its fine grain size. The mixed oxides originating from red mud could be possible alternatives to the commercial catalysts used for hydrodechlorination reactions [4,21–24].

We report here our investigations concerning the activity and selectivity in the gas-phase hydrogen treatment of a range chlorohydrocarbons such as 1,2-dichloroethane (DCE), 1,1,2-trichloroethane (TRCE), 1,1,2,2-tetrachloroethane (TCE), trichloroethene (TRCEE) and

1,1,2,2-tetrachloroethene (TCEE) over metal oxides such as Fe<sub>2</sub>O<sub>3</sub> (crystalline and amorphous), Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, complex mixed oxide derived from red mud in comparison with iron-containing modified zeolite Fe-ZSM5.

## 2. Experimental

### 2.1. Materials

The chlorine-containing hydrocarbons used in this study (DCE, TRCE, TCE, TRCEE and TCEE) were supplied by Sigma–Aldrich Hungary.

Pure iron oxide, used as catalyst, was synthesized by precipitation from iron nitrate solution with ammonium hydroxide solution. Depending on the temperature and reaction time crystalline or amorphous forms could be prepared.

The Al/Fe-mixed oxide was synthesized by coprecipitation from aluminum nitrate and iron nitrate solutions followed by calcination at 500 °C for 4 h, and the alumina supported iron oxide was prepared by impregnating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with iron nitrate solution followed by heat treatment at 500 °C. The Fe content of this sample was 5 wt.%, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was supplied by Aldrich; the BET surface area was 155 m<sup>2</sup>/g.

The red mud utilized for catalyst preparation was the original waste from the Ajka Aluminum Industry of Hungary. The wet red mud was filtered, dried at 100 °C followed by calcination at 500 °C for 4 h. The average composition of the Hungarian red mud is displayed in Table 1.

For comparison, we studied the catalytic activity of MFI type zeolite (Si/Al=40) containing Ni or Fe introduced by solid-phase ion exchange [25]. The first step of the solid-state method was 24 h stirring of 10 g Na-ZSM-5 zeolite in 0.5 dm<sup>3</sup> solution of NH<sub>4</sub>Cl at 0.5 mol/dm<sup>3</sup> concentration. After filtration and washing, stirring was repeated. The sample was filtered, washed, dried and heated at 600 °C for 4 h to decompose NH<sub>4</sub><sup>+</sup> ions into gas-phase NH<sub>3</sub> and H<sup>+</sup>. The product was H-ZSM-5, which was mixed with 5% Fe-equivalent FeCl<sub>3</sub>·5H<sub>2</sub>O and mixture was maintained at 500 °C for 4 h.

### 2.2. Methods

The composition of the fresh and the used catalysts were determined by classical chemical analysis and X-ray fluorescence method after digestion by K<sub>2</sub>CO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> + Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (1:1:1 weight ratio) mixture at 1000 °C.

The crystal structure of the catalysts before and after the reactions was characterized by powder X-ray diffraction measurements using a DRON3 apparatus in the reflection angle range of 2 $\theta$  = 3–65°. The surface area of the catalysts was measured with nitrogen adsorption on a Quantachrome NOVA2200 equipment. The pore size distribution has been calculated from the nitrogen isotherms.

Table 1  
The average composition of Hungarian red mud

Al <sub>2</sub> O <sub>3</sub>	16–18 wt.%	CaO	0.5–3.5 wt.%
Fe <sub>2</sub> O <sub>3</sub>	33–48 wt.%	V <sub>2</sub> O <sub>5</sub>	0.2–0.3 wt.%
SiO <sub>2</sub>	9–15 wt.%	P <sub>2</sub> O <sub>5</sub>	0.5–1 wt.%
TiO <sub>2</sub>	4–6 wt.%	CO <sub>2</sub>	2–3 wt.%
Na <sub>2</sub> O	8–12 wt.%	S	0.15–0.30 wt.%
MgO	0.3–1 wt.%	F	0.10–0.15 wt.%

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