



Low-temperature combustion of chlorinated hydrocarbons over CeO₂/H-ZSM5 catalysts

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ARTICLE INFO

Article history:

Received 19 September 2011

Received in revised form 1 December 2011

Accepted 16 December 2011

Available online 27 December 2011

Keywords:

Chlorinated VOCs

Catalytic oxidation

1,2-Dichloroethane

Supported cerium oxide catalyst

H-ZSM5 zeolite

ABSTRACT

The performance of various CeO₂/H-ZSM5 catalysts was evaluated for the oxidation of one of the most common chlorinated pollutants found in waste streams, namely 1,2-dichloroethane. The supported samples with varying CeO₂ loading (6–50 wt.%) were prepared by impregnation and subsequently calcined at 550 °C. Structural, morphological and physico-chemical changes caused by the CeO₂ addition were analysed by X-ray diffraction, transmission electronic microscopy, N₂-physisorption, temperature-programmed desorption of ammonia and temperature-programmed reduction with hydrogen. The enhancement of the catalytic behaviour of the resulting samples with respect to plain H-ZSM5 could be accounted for on the basis of the synergetic role played by oxygen mobility and acid sites. Hence, an optimum cerium loading of 11 wt.% was found with a *T*₅₀ value around 210 °C. At 350 °C, where conversion of the chlorinated feed is about 99%, the major oxidation products were carbon oxides and hydrogen chloride with a reduced presence of chlorinated by-products and molecular chlorine. A relatively good catalytic stability was noticed during 80 h time on line.

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1. Introduction

The increased production and application of chlorinated volatile organic compounds (VOCs) have caused increased concerns over proper disposal and control of these hazardous waste materials. These compounds have a high chemical and thermal stability, and tend to accumulate in the environment. Besides causing localised odour problems, these pollutants are responsible for the increase in ground-level ozone concentrations and the formation of secondary organic aerosols as well. Moreover, some compounds have a carcinogenic, teratogenic or mutagenic character. For this reason, in recent years legislation has been introduced in many countries setting very low emissions limits in process exhaust gases [1].

Chlorinated VOCs have been produced commercially and used for many purposes by the chemical industry including the manufacture of herbicides, plastics, and solvents. Uses outside the chemical industry include solvent degreasing in the automotive and aerospace industries, and dry cleaning solvents in the garment industries and precision solvent cleaning in the electronic industries. When VOC emissions cannot be avoided, they ought to be controlled by an appropriate end-of-pipe-device. If there

is no interest in recovering VOCs they are usually destroyed by deep oxidation. However, as the VOC concentration is usually very low (below 1000 ppm), direct combustion may not be appropriate. In conventional incineration methods temperatures exceeding 700 °C are required to obtain complete decomposition. This would require a large amount of extra fuel to maintain the flame temperature and may produce toxic substances and NO_x. Furthermore, the combustion of chlorinated hydrocarbons presents additional complications. For instance, chlorine-containing materials are known to inhibit flame propagation and have low heats of combustion. As a result, development of low-temperature (in the range 300–550 °C) processes for chlorinated waste disposal can offer significant improvements over traditional thermal oxidation [2]. Catalytic deep oxidation is more selective and, as it requires less heating, is more cost effective than direct combustion for treating oxygen-containing waste gases. As large gas volumes have to be typically treated, this catalytic approach has to be performed at very high space velocity (>10,000 h^{−1}) and thus requires a very active catalyst. A catalytic combustion process, if properly designed, must lead to the complete destruction of all kinds of chlorinated VOC including the harmful by-products, which can be produced by an incomplete destruction of the starting chlorocarbon.

Supported noble-metal catalysts as well as (supported) metal oxide catalysts are commercially applied for the oxidation process. Alumina is most frequently employed as a carrier. Noble metals

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