



Cu and Co modified beta zeolite catalysts for the trichloroethylene oxidation



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ABSTRACT

In this work we have studied for the first time the catalytic activity for the oxidation of trichloroethylene (TCE) of Cu and Co beta zeolites. The results show that they are active and selective towards CO₂, obtaining a better selectivity than that reached with conventional H-zeolites. The copper and cobalt zeolites have been prepared by different methods. It was found that their activity depends on the metal and on the preparation procedure. The most active catalyst was the Cu-BEA prepared by ion exchange (T_{50%} = 310 °C and T_{90%} = 360 °C). This catalyst has the highest ammonia adsorption capacity (as a measurement of the acidity) and it was the only tested material in which the Me²⁺ was completely reduced in a standard H₂-TPR experiment (indicative of its important redox properties). Thus, the enhanced activity of the Cu-exchanged zeolite was associated to the presence of strong acid sites in the zeolite and to the redox properties of the copper ion exchanged. The catalyst was stable at 300 °C for almost 70 h without any important deactivation. This was related to the oxidative properties of the copper that avoid the formation of coke on the strong acid sites of the zeolite. On the other hand, zeolites with the transition metal incorporated into the zeolite framework by hydrothermal synthesis showed lower catalytic activity, probably because the formation of small oxide particles with much less interaction with the silicate framework, that results in a lower redox activity of the transition metals. It has been shown that a proper combination of acidity, redox properties and metal-zeolite interaction is necessary in order to prepare an active and selective zeolite catalyst for the TCE oxidation.

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1. Introduction

Volatile organic compounds (VOCs) are defined as any organic compound having at 293.15 K, a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use (Council Directive 1999/13/EC of 11th March 1999). They are widespread applied in industry, mainly as solvents. Nevertheless, VOCs are considered as pollutants because their toxicity and their contribution to the formation of low-level ozone (photochemical smog) and to the ozone layer depletion (mainly the CFC). Trichloroethylene (TCE) is a common chlorinated VOC that was a dominant cleaning product in the 70's and now is commonly used for the degreasing of mechanical parts and dry-cleaning [1]. It has been classified as probably carcinogenic to humans by the Inter-

national Agency for Research on Cancer [2]. For these reasons the control of the TCE emissions is an important issue for environmental protection.

Thermal incineration has become the conventional method of reducing VOC emissions from industrial processes. It has proved to be successful in many processes but it has major drawbacks [3]. First, temperatures must reach over 1000 °C for the complete pollutant destruction making it an uneconomical process. In addition the high temperatures reached in this process generate higher quantities of NO_x and finally, this technique is not very effective with low pollutant concentration streams.

Catalytic oxidation of VOCs is a realistic contender to the conventional method [4,5]. It requires lower temperatures (250–550 °C), generating less energetic costs and preventing the formation of non-desired by-products. Several catalysts, as metal oxides [6–11], bronzes [12] and noble metals supported on different materials [13] have been studied for the catalytic oxidation of chlorinated organic volatile compounds (CVOCs), but they have problems related with the catalyst deactivation and with the formation of toxic by-products [14]. Other materials, as acid zeolites have been described as alternative catalysts for the trichloroethy-

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lene oxidation [15]. However, after a certain period of time, acid zeolites deactivate due to coke deposition and chlorine attack to the acid sites [16]. In these catalysts, Brønsted acidity plays an important role, controlling the oxidative activity of the zeolites [15,17]. It was found [17,18] that dealumination of Y zeolite by ammonium hexafluorosilicate was a procedure that can improve the catalytic activity of H-Y zeolites for chlorinated VOC decomposition, due to the strong Brønsted sites formed in the dealumination treatment.

Other strategies were based in a combination of transition metals and zeolites [19–21]. In this way, Divakar et al. [22] studied the catalytic activity of ZSM-5 and Beta zeolites with Fe and they found that all the catalysts were active for the trichloroethylene oxidation, but the results obtained depended on the catalyst preparation procedure. Huang et al. [23] studied the synergy between Cr_2O_3 - CeO_2 and USY zeolite on the catalytic performance, showing that the interaction between chromium and cerium improves the mobility of oxygen species, favouring the oxidation of the chlorinated volatile organic compounds. These results show that the interaction of the transition metal and the zeolite improves the catalytic activity of the material. This interaction depends on the way the transition metal is incorporated to the zeolite structure and this has never been previously studied for this reaction. In this work we have studied this topic by using different catalysts based on beta zeolites for the TCE oxidation.

Beta zeolite was chosen because it can be synthesized with a wide range of Si/Al molar ratios and other elements different from Si and Al can be incorporated to the material. It is the only high-silica zeolite possessing a three-dimensional intersecting channel system of large pores with high thermal and hydrothermal stability, high diffusion capacity and low steric restrictions, assuring the absence of diffusional limitations. In addition, transition metals can be added to the zeolite by different post-synthesis methods (as ion exchange, incipient wetness impregnation, etc.) or they can be integrated in the zeolite framework during the synthesis process. Some papers have reported [24–27] the high activity of the latter zeolites in different redox reactions. Thus, it could be expected that these catalysts are also active for the TCE oxidation. Furthermore, by comparing the activity of zeolites with transition metals incorporated by different processes, we can study the influence of the metal-zeolite interaction in the catalyst behaviour. In this paper, Cu and Co zeolites have been prepared by ion exchange and by hydrothermal synthesis and the catalytic activity of these materials for the TCE oxidation reaction has been studied and compared with that of H-BEA zeolite.

2. Materials and methods

2.1. Catalysts preparation

A commercial acid beta zeolite (CP811, PQ Zeolites B.V.) was used as a reference material. Some catalysts were prepared from this parent material by adding copper or cobalt to the zeolite by a conventional ion-exchange procedure. The metal exchange was performed in an aqueous solution containing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the adequate concentration to achieve the desired amount of metal on the zeolite and with a solid/liquid ratio of 1/150. The metal exchange was at 80 °C for the Co-samples and at room temperature for the Cu-samples. After 24 h under mechanical stirring, the solutions were washed, filtered and dried at 100 °C [28]. In the case of the Cu-sample, before washing, a 0.1 M NH_4^+ solution was added to increase the pH of the solution up to 6–7. After drying the samples, they were heat-treated at 450 °C for 4 h.

In other group of catalysts, copper or cobalt were added to the zeolite framework by hydrothermal synthesis. In order to prepare the catalysts, a procedure based on that published in refer-

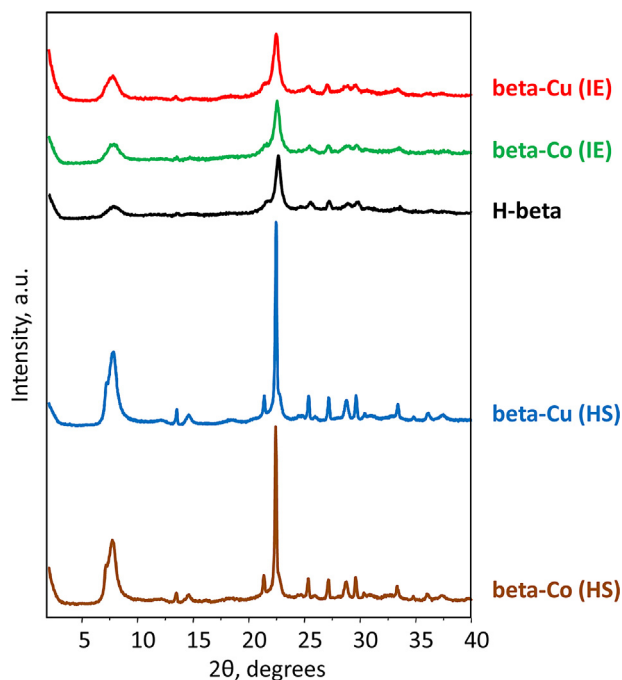


Fig. 1. XRD patterns of H-beta, beta-Cu (IE), beta-Cu (HS), beta-Co (IE) and beta-Co (HS).

ence [29] was followed. In particular, tetraethylorthosilicate (TEOS, Merck) was hydrolysed in an aqueous solution of tetraethyl ammonium hydroxide (TEAOH, 35%, Aldrich). Then, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) dissolved in deionized water was added and the mixture was stirred at room temperature in order to evaporate the ethanol produced during the hydrolysis of TEOS. After that, HF was added to the mixture and finally a suspension of zeolite beta seeds in water was added. The final gel composition was:



where MeO represents the metal (Cu or Co) expressed as the corresponding oxide.

The solid obtained was transferred to a Teflon-lined stainless-steel autoclave and heated up to 140 °C while being rotated at 60 rpm. After 7 days at the crystallization temperature, the autoclave was quenched, the content filtered and the solid washed with deionized water, dried at 100 °C and calcined at 580 °C for 3 h.

All catalysts were pelletized, and then the pellets were crushed and sieved to obtain grains of 0.25–0.45 mm in diameter. Materials were named as beta-Cu (X) or beta-Co (X), where X corresponds to the preparation method of the samples, i.e. IE (ion exchange) and HS (hydrothermal synthesis).

2.2. Catalysts characterization

The surface areas of the different catalysts were measured on an ASAP 2010 instrument (Micromeritics) using the BET method from the nitrogen adsorption isotherms at –196 °C.

Powder X-ray diffraction patterns (XRD) were collected using an X'Pert-Pro diffractometer (Panalytical) equipped with an X'Celerator detector and using Ni-filtered $\text{Cu K}\alpha$ radiation.

The chemical composition of the samples was measured by inductively coupled plasma (ICP-OES) in a Varian 715-ES ICP-Optical Emission Spectrometer.

Temperature programmed reduction (TPR) experiments were carried out using a TPD-TPR Autochem 2910 analyzer equipped with a thermal conductivity detector. The reduction of the sam-

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