

# Improvement of toluene catalytic combustion by addition of cesium in copper exchanged zeolites

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## Abstract

HY and HMF1 zeolites exchanged with copper and cesium have been studied for the catalytic combustion of toluene (800 ppm) with air. The catalysts activity has been analyzed by comparison of light-off curves and in both Cu zeolites, the addition of Cs leads to a decrease of the light-off temperature by 50 °C. Temperature-programmed reduction (H<sub>2</sub>-TPR) and EPR studies have evidenced clear differences in the characteristics of the copper species both in the presence and absence of Cs co-cations. These differences account for the nature of the active centers in the Cu zeolites for the toluene oxidation. The position and geometry of the copper ions in the zeolite matrix are of great significance for the redox behavior and activity for toluene oxidation. In both MFI and FAU structures, the bulky Cs co-cations are located in the more accessible main zeolite pores, forcing the copper ions to occupy the most stable, but less accessible positions within each structure. In the case of the MFI zeolite, the EPR study revealed that the Cs exchange resulted in an increased abundance in the number of square pyramidal Cu<sup>2+</sup> ions relative to the other Cu environments. Cs co-cations also lead to an increase in the reducibility of the copper ions mainly due the reduction of protons in Cu, Cs-containing samples.

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## 1. Introduction

Catalytic oxidation has been identified as one of the most promising ways to reduce volatile organic compounds (VOCs) emissions to meet the requirements of air pollution control regulations [1]. Due to the low contaminant level and the large volume of gas to be treated it is necessary to use highly active catalysts operating at low temperatures. Noble metals such as Pt and Pd supported on alumina and silica are well established as efficient catalysts for complete combustion of VOCs [2,3], but they are relatively expensive. Therefore, cheaper catalytic materials, involving transition metal oxides are becoming of increasing importance. Catalysts based on transition metals (Ni, Cu, Co, Cr, Mn and Fe) oxides have been intensively studied [4,5], but the activity shown by these oxides is generally lower

than that of noble metal catalysts. Nevertheless, these types of catalysts are thermally more stable and also more resistant to poisoning by compounds containing sulphur or chlorine [6] and depending on the nature of the VOC, they can be more active than noble metals for VOC destruction [7]. It is therefore evident that, if high activity transition-metal-based catalysts can be developed for VOC destruction, these will be preferred.

The materials used to support the transition metals have also an important role on catalytic properties for combustion. It is known that materials with high thermal stability, resistance to humidity, specific surface area and ability to stabilize the metal particles in the porous structure are desired [8]. Zeolites have been claimed as promising supports to stabilize transition metals with great potential as oxidation catalysts [9]. The availability of zeolites with several porous structures, different composition and hydrophobicity degree, as well as the possibility to control the acidic properties and location of exchanged cations have contributed to increase the advantages of zeolites relative to other traditional support materials [10].

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In this work, the chosen VOC probe molecule was toluene, which is a commonly used solvent in chemical and processing industries. Therefore, toluene emission in the atmosphere need to be controlled. In a systematic study of transition metals supported on alumina, copper was found to be the most promising catalyst for complete oxidation of aromatics [11]. Our earlier studies [12] have also indicated that among the metals Cr, Co, Cu and Ni ion-exchanged into Y zeolite, copper was found to be the most promising for the catalytic combustion of toluene. Moreover, the presence of sodium co-cations in CuY zeolites was shown to increase the combustion efficiency [13]. Bulánek et al. [14] have also observed that propane oxidation was strongly influenced by the type of co-cation ( $\text{Na}^+$  versus  $\text{H}^+$ ) in Cu-zeolites. A positive influence of potassium on the activity of Cu–K/TiO<sub>2</sub> catalysts was also found for oxidation of soot particles [15]. There is also some information about the stabilizing effect of promoters such as La and Ce on the catalytic activity of CuZSM-5 in the total oxidation of ethane [16].

In spite of all the studies reporting the different factors that influence redox properties and catalytic behavior of Cu-zeolites, the nature of the active sites for total oxidation of hydrocarbons has not been completely elucidated. Some authors [16,17] correlate the catalytic activity in the complete oxidation with the concentration of isolated  $\text{Cu}^{2+}$  in a square planar coordination, while others [14] have shown that well-dispersed CuO species exhibited much higher oxidation activity and reducibility compared to the exchanged Cu ions.

In this work, HY and HZSM-5 (HMFI) zeolites exchanged with copper (1–5 wt.%) and cesium (5–10 wt.%) have been studied as catalysts for the combustion of toluene (800 ppm) with air. The effect of the Cs co-cation on the state, location and reducibility of the copper ions in the zeolite matrix were evaluated in order to investigate the nature of the species that are involved in the oxidation reactions.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The CuHY and CuCsHY series of catalysts were prepared using the same parent Y zeolite (CBV500) provided by PQ Zeolites in a protonic form and with a Si/Al molar ratio of 2.5. The MFI zeolite with a Si/Al molar ratio of 19 was provided by UOP in the H form. Cesium was introduced by aqueous ion exchange with a solution 0.07 M of cesium acetate. The ion exchange was carried out using a ratio volume of solution/weight of zeolite of 70 mL g<sup>-1</sup>, under reflux and continuous stirring for 2 h at 80 °C. After filtration and drying, the samples were submitted to a calcination under air flow (3 L h<sup>-1</sup> g<sup>-1</sup>), from room temperature to 500 °C, at 5 °C min<sup>-1</sup>, for 2 h. Furthermore, copper was added with an aqueous copper (II) acetate solution, which contained the appropriate copper amount. The ion exchange was also carried out using a ratio volume of solution/weight of zeolite of 70, at room temperature and continuous stirring for 24 h. At the beginning of the ion-exchange process an aqueous ammonia solution (3 M) was used to stabilize the pH at 7.5. After washing with distilled water,

filtration and drying at 100 °C, the catalysts were calcined under air flow (4 L h<sup>-1</sup> g<sup>-1</sup>), from room temperature to 500 °C (at 5 °C min<sup>-1</sup>) for 8 h.

The chemical analysis of the samples was performed by inductively-coupled plasma (ICP) and atomic absorption spectroscopy to obtain Cs and Cu contents. The crystallinity of the zeolites and the possible formation of copper oxides was evaluated from the powder XRD patterns recorded on a Rigaku Geigerflex diffractometer employing Cu K $\alpha$  radiation filtered by Ni.

The copper catalysts were characterized by hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR). The TPR measurements were performed after pretreatment of the catalysts. The calcined samples (130 mg) were heated under air flow (30 mL min<sup>-1</sup>) at 550 °C for 1 h and then cooled to room temperature. Reduction of the catalysts was carried out by flowing 30 mL min<sup>-1</sup> of a H<sub>2</sub> (5 vol.%) / Ar mixture and raising the temperature from room temperature to 1000 °C at 10 °C min<sup>-1</sup>. The change in hydrogen concentration was continuously monitored by a thermal conductivity detector. The water formed during reduction was trapped in a cryogenic trap. To determine the total H<sub>2</sub> consumption and the quantities of H<sub>2</sub> consumed under each individual reduction process, the deconvolution of the peaks was performed using the commercial software package Peak-Fit (Peak Separation and Analysis Software, SPSS Science).

The toluene adsorption capacity of the samples was determined by thermogravimetry using a SETARAM TG-DSC 92 thermobalance. The samples were pretreated under air flow, from room temperature to 550 °C, at 5 °C min<sup>-1</sup>, for 1 h and then cooled at 70 °C. This temperature was maintained during the adsorption process. A gas mixture (50 mL min<sup>-1</sup>) composed of toluene (1000 ppm) and N<sub>2</sub> passed through the catalysts and the mass increase was followed as a function of time until stabilization of weight. Then, the toluene flow was stopped and the desorption was done under nitrogen flow from 70 to 600 °C at 5 °C min<sup>-1</sup>. Loss of mass and heat flow were followed as a function of temperature.

The EPR spectra of the freshly prepared and dehydrated CuHMFI and CuCsMFI were all recorded at low temperature (130 K) on a cw-Bruker EMX spectrometer, operating at 9.4 GHz (X band) frequency, 100 kHz field modulation and equipped with an ER-4119HS Bruker high-sensitivity cavity. For dehydration studies, ca. 0.4 g of each sample was placed into a quartz suprasil EPR tube containing a suitable adaptor for connection to a vacuum manifold. The samples were evacuated successively at 100, 200, 300, 400 and 500 °C (30 min at each temperature), under dynamic vacuum (10<sup>-4</sup> Torr). To estimate the population of Cu<sup>2+</sup> species present in different environments for CuHMFI and CuCsMFI, the low field component of the  $g_{\parallel}$  peaks were deconvoluted using a Gaussian distribution.

### 2.2. Catalytic tests

The catalytic tests were carried out at atmospheric pressure in a fixed-bed flow reactor. A tubular quartz reactor with 12 mm diameter was placed inside an electrical furnace provided with

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