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Performance of supported catalysts based on a new copper vanadate-type precursor for catalytic oxidation of toluene

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Abstract

A new copper vanadate precursor with the formula $NH_4[Cu_{2.5}V_2O_7(OH)_2]\cdot H_2O$ was synthesized and deposited on two different supports, ZSM-5 and amorphous SiO_2, by a hydrothermal method or by mechanical mixture. The catalytic behaviour was evaluated in the total oxidation of toluene and the characterization was performed by H_2-temperature-programmed reduction (H_2-TPR), thermogravimetric analysis, elemental analysis, UV–vis diffuse reflectance spectroscopy and X-ray diffraction.

It was found that the copper vanadate phase comprises two mixed oxides, one of them crystalline, the Ziesite phase, and the other one amorphous. The supported catalysts presented a content of copper vanadate phase of about 9–11 wt.%.

The copper vanadate deposited on ZSM-5 by the hydrothermal method evidences the best performance in the oxidation of toluene. This behaviour can be associated with the smaller size and higher dispersion of the particles on the support, which was confirmed by their better reducibility and higher band gap energy value compared with the other series of studied catalysts.

Keywords: VOCs; Copper vanadate; Toluene oxidation; ZSM-5

1. Introduction

Volatile organic compounds (VOCs) are some of the main atmospheric pollutants and toluene is recognized as one of the most representatives. Environmental legislation has established stringent regulations to control VOC emissions [1]. Catalytic oxidation is a very promising process for VOCs elimination, since it operates at temperatures much lower than those required for thermal incineration. The most commonly used catalysts are based on noble metals and transition metal oxides [2,3]. Catalysts based on transition metals (Ni, Cu, Co, Cr, Mn and Fe) oxides have been intensively studied [2–5], but the activity shown by these oxides is generally lower than noble metals catalysts. Nevertheless, this type of catalysts is thermally more stable and also more resistant to poisoning by compounds containing sulphur or chlorine [3,6]. The base metal oxides are much cheaper than noble metals, so they are usually prepared with a higher metal content and added at a higher catalyst loading, leading to an increased number of active sites in the metal oxide bed. This results in a catalyst that can be as effective as Pt for the catalytic combustion of some hydrocarbons [7,8]. Among several metal oxides, CuO has shown good performances for the catalytic incineration. The catalytic incineration of toluene over CuO species impregnated on different supports (γ-Al_2O_3, CeO_2, TiO_2 and V_2O_5) was investigated and CeO_2 support followed by γ-Al_2O_3 produced the most active catalysts [8].

Previous studies using several transition metals (Cr, Co, Cu and Ni) exchanged in zeolites [9], evidenced copper as the most performing transition metal ion for the catalytic combustion of toluene. Moreover, the presence of Cs co-cations in CuY and Cu-ZSM-5 zeolites was shown to increase their combustion efficiency [10,11]. Vanadium/zeolite catalysts also have demonstrated promising results [12], suggesting some kind of strong interaction between the vanadium ions and the zeolite [13].

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The reported results encourage the replacement of the most widely used noble metals (Pt, Pd) supported on alumina, silica and zeolites, by cheaper transition metals.

On another hand, while exploring new materials with good potential catalytic properties, a series of copper vanadates was synthesized, belonging to the so called Φ_z family [14]. This structure is characterized by containing Brucite-type layers, connected by pyrovanadate groups [15,16]. These lamellar materials have compensation cations and water molecules between the layers. In previous experiments, a good performance of this type of material as precursors of catalysts was found for the combustion of VOCs. However, when a lamellar precursor is calcined in order to obtain the catalyst, the inter layer molecules are released and the structure collapses, producing a catalyst with low surface area. With the aim to improve the textural characteristics and the catalytic performance of these materials, one possibility is to support them on a carrier with high surface area. We tried to use mesoporous materials, but the hydrothermal and pH conditions of the precursor synthesis destroy the supports. Microporous zeolites, like ZSM-5, are prepared under similar conditions as such precursors; for this reason, they could keep their structure under the synthesis conditions for incorporation of the precursor.

In this work, we used a new Φ_z-type copper vanadate as catalyst precursor and we incorporated this phase on a ZSM-5 zeolite. In order to compare the influence of the support, the precursor was also supported on amorphous SiO_2. The precursor and the catalysts were characterized by powder X-ray diffraction (XRD), chemical analysis, thermogravimetry/differential scanning calorimetry (TG/DSC), diffuse reflectance spectroscopy UV–vis and hydrogen temperature-programmed reduction (H_2-TPR). Then the catalysts were tested in toluene combustion. Toluene was selected as a VOC probe molecule because it is a commonly used solvent in chemical and processing industries and controlling its emission in the atmosphere is becoming relevant.

2. Experimental

2.1. Catalysts preparation

The precursor, a new copper vanadate, was prepared by a hydrothermal method following the procedure of Hoyos [16]. The bulk catalyst (called CuV bulk) was obtained by calcining the precursor at 320 °C. For the synthesis of the precursor, V_2O_5 (Aldrich, 98%) was added to a solution previously prepared with distilled water and NH_4OH solution (Fluka, ∼25%). Then, the suspension was homogenized for 45 min. Separately, $CuCl_2{\cdot}2H_2O$ (Merck, 99%) was dissolved in distilled water. The copper solution was then added to the vanadium mixture, forming a gel, which was magnetically stirred for 2 h. The final pH of the gel was 10 and its molar ratio was 1.0 V_2O_5:2.5 $CuCl_2$:4.7 NH_4OH:538 H_2O. Subsequently, the mixture was transferred to a Teflon-lined autoclave and it was heated at 170 °C for 24 h. The solid was recovered by filtration and washed with distilled water until a neutral pH was reached. Finally, the solid was dried at 100 °C.

Table 1
TGA data and amount of precursor and active copper vanadate phase in the supported catalysts

Catalyst[a]	Weight loss at 400 °C (%)	Weight loss at 322 °C (%)	Precursor, (wt.%)	CuV (wt.%)
CuVZSM-5(h)	6.2	4.6	10.9	9.2
CuVZSM-5(m)	6.3	6.1	13.0	11.0
CuVSiO$_2$(m)	1.5	1.4	12.7	10.3

[a] h: Hydrothermal method, m: mechanical mixture.

The new copper vanadate precursor was incorporated into ZSM-5 following the same method described above, preserving the molar ratio, but using a mass ratio of V_2O_5/ZSM-5 of 0.04. ZSM-5 (in acid form and with Si/Al ratio = 19) was added immediately after formation of copper vanadium gel. The solid that was calcined at 320 °C, will be called hereafter CuVZSM-5(h). Two other catalysts were prepared, especially for comparative studies, by making a mechanical mixture of ZSM-5 or SiO_2 with the amount of copper vanadate precursor reported on Table 1 and then calcined at 320 °C. Those catalysts are called CuVZSM-5(m) and CuVSiO$_2$(m). Bulk catalyst (CuV bulk) and samples of pure oxides V_2O_5 (Aldrich, 98%) and CuO (Aldrich, 99%) as well as a mixture of both these oxides (with the same Cu/V proportion than CuV bulk), were also used for catalytic tests.

2.2. Catalysts characterization

For the precursor composition and bulk catalyst, the vanadium content was measured by atomic emission spectroscopy with a plasma source in a Perkin-Elmer Optima 2000 V instrument, the copper content by atomic absorption in a Perkin-Elmer Analyst 300 instrument and nitrogen by elemental analysis in a Fisons Instruments EA 1108 CHNS equipment.

The uncalcined precursors, both in the supported and unsupported forms, were analysed by thermogravimetry with simultaneous differential scanning calorimetry in a Setaram TG-DSC 92 equipment, under an air flow of 30 mL min^{-1} and heating rate of 10 °C min^{-1} up to 800 °C.

The XRD powder patterns were obtained in a Bruker AXS AdvanceD8 diffractometer using Cu Kα radiation and operated at 40 kV and 30 mA. The scanning range was set from 5° to 40° (2θ) with a step size of 0.02 s. The phases were identified using the "Powder Diffraction File (PDF-2)" database.

N_2 adsorption–desorption isotherms were obtained at −196 °C on a Micrometrics ASAP 2010 instrument, after outgassing the samples at 150 °C (350 °C for ZSM-5 alone).

Temperature-programmed reduction with hydrogen (H_2-TPR) was carried-out after pre-treatment of the catalysts. The catalysts were heated under argon flow (30 mL min^{-1}) at 200 °C for 40 min and then cooled down to room temperature. Reduction of the catalysts was carried out by flowing 30 mL min^{-1} of a H_2 (5 vol.%)/Ar mixture and raising the temperature from ambient up to 700 °C at 5 °C min^{-1}. The change in hydrogen concentration was continuously monitored by a thermal conductivity detector. The water formed during reduction was trapped in a cryogenic trap.