

# 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  $\text{NH}_4[\text{Cu}_{2.5}\text{V}_2\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O}$  was synthesized and deposited on two different supports, ZSM-5 and amorphous  $\text{SiO}_2$ , 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  $\text{H}_2$ -temperature-programmed reduction ( $\text{H}_2$ -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.

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## 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 con-

taining 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 ( $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ ) was investigated and  $\text{CeO}_2$  support followed by  $\gamma\text{-Al}_2\text{O}_3$  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  $\Phi_z$  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  $\Phi_z$ -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<sub>2</sub>. 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<sub>2</sub>-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<sub>2</sub>O<sub>5</sub> (Aldrich, 98%) was added to a solution previously prepared with distilled water and NH<sub>4</sub>OH solution (Fluka, ~25%). Then, the suspension was homogenized for 45 min. Separately, CuCl<sub>2</sub>·2H<sub>2</sub>O (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<sub>2</sub>O<sub>5</sub>:2.5 CuCl<sub>2</sub>:4.7 NH<sub>4</sub>OH:538 H<sub>2</sub>O. 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 <sup>a</sup>	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 <sub>2</sub> (m)	1.5	1.4	12.7	10.3

<sup>a</sup> 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<sub>2</sub>O<sub>5</sub>/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<sub>2</sub> 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<sub>2</sub>(m). Bulk catalyst (CuV bulk) and samples of pure oxides V<sub>2</sub>O<sub>5</sub> (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<sup>-1</sup> and heating rate of 10 °C min<sup>-1</sup> up to 800 °C.

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

N<sub>2</sub> 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<sub>2</sub>-TPR) was carried-out after pre-treatment of the catalysts. The catalysts were heated under argon flow (30 mL min<sup>-1</sup>) 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<sup>-1</sup> of a H<sub>2</sub> (5 vol.)/Ar mixture and raising the temperature from ambient up to 700 °C at 5 °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.

Diffuse reflectance (DR) spectra in the UV–vis region were obtained in a Varian Cary 5000 UV–vis–NIR spectrophotometer, equipped with a diffuse reflectance accessory (praying mantis, Harrick), in the 200–800 nm range. CuVZSM-5(h) and CuVZSM-5(m) spectra were obtained using ZSM5 as reference. Spectra of CuVSiO<sub>2</sub>, bulk CuV and V<sub>2</sub>O<sub>5</sub> were recorded using SiO<sub>2</sub> as reference.

The reflectance spectra were digitalized, converted into the Schuster–Kubelka–Munk (SKM) function,  $F(R_{\infty})$ , and presented versus wavelength. The SKM function,  $F(R_{\infty})$ , is calculated from the reflectance, at each wavelength, using the expression:  $F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$ , where  $R_{\infty}$  is the ratio of the intensity of the light reflected by the sample to the one reflected by a standard.

### 2.3. Catalytic tests

Toluene oxidation was carried-out at atmospheric pressure in a fixed bed reactor, using 300 mg of catalyst. The reactant gas mixture, air containing toluene (800 ppm), was prepared by passing air through a saturator containing toluene, which was kept at  $-3^{\circ}\text{C}$ , and then, diluted with another air stream. The reactant mixture was supplied with a flow rate of  $15\text{ L h}^{-1}$ . The feed and the reaction products were analysed by an on-line gas chromatograph, equipped with a thermal conductivity detector (TCD) and flame ionisation detector (FID) in series. The hydrocarbons and the carbon dioxide were analysed with a Poraplot Q capillary column and carbon monoxide with a Molecular Sieve 5A capillary column, both columns being connected in parallel.

The catalytic activity was evaluated in terms of toluene conversion and conversion to CO<sub>2</sub>, in the temperature range between 200 and 400 °C (or 320 °C for copper vanadates-based catalysts). At each reaction temperature, the conversions were analysed after 1 h time-on-stream.

## 3. Results and discussions

### 3.1. X-Ray diffraction

The powder patterns for the precursor and bulk catalyst are shown in Fig. 1. The precursor pattern indicates that the new  $\Phi_z$  copper vanadate phase was obtained [16]. When this lamellar material is calcined at 320 °C, a single phase is transformed into a mixture of phases identified as Ziesite (Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, PDF 26-569) and an amorphous copper vanadium oxide phase. The temperature used for the calcination of the precursor was chosen based on a previous work [17] that has shown that the composition of the samples depends on the calcination temperature, and the structural differences evidenced by the several samples influence their catalytic behaviour for total oxidation of toluene, being the best catalytic performance obtained with the material calcined at 320 °C. As it was discussed and reported elsewhere [17], the structure of the Ziesite phase possesses pyrovanadate groups connected to copper polyhedrons in square pyramidal coordination with oxygen atoms, generating a three-dimensional structure with channels along the *c* axis.

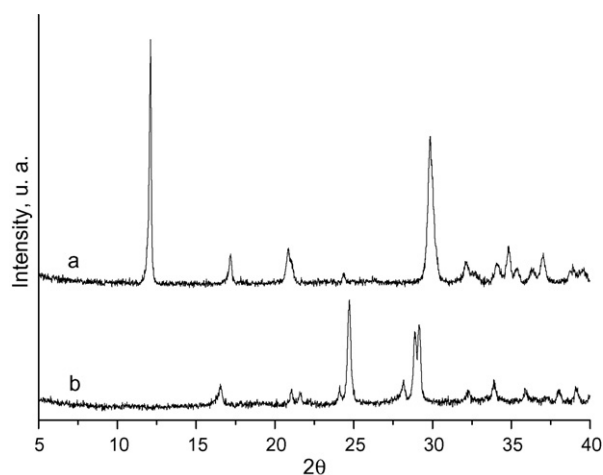


Fig. 1. X-ray diffraction pattern: (a) precursor, (b) CuV bulk.

XRD patterns of supports and catalysts are shown in Fig. 2. The synthesis of copper vanadate by the hydrothermal method on ZSM-5 did not alter the structure of zeolite, as shown by the diffractograms obtained for the ZSM-5-based catalysts. One of the main reflections corresponding to copper vanadate can be identified in the patterns (as indicated with the arrows), although several peaks are overlapped with those of the support and the amount of the copper vanadate on the support is not large. The presence of the CuV phase on SiO<sub>2</sub> can be more clearly observed, because there is no overlapping with peaks from the support.

### 3.2. Catalysts composition and thermal analysis

The elemental composition of the precursor measured experimentally is Cu 37, V 22 and N 3.1 wt.% (in weight base). For bulk copper vanadate, the weight percentages are Cu 41 and V 24 wt.%. The total weight loss in the TGA of the precursor is about 12%, corresponding to volatile compounds like water and ammonia. Based on this information, the formula of the precur-

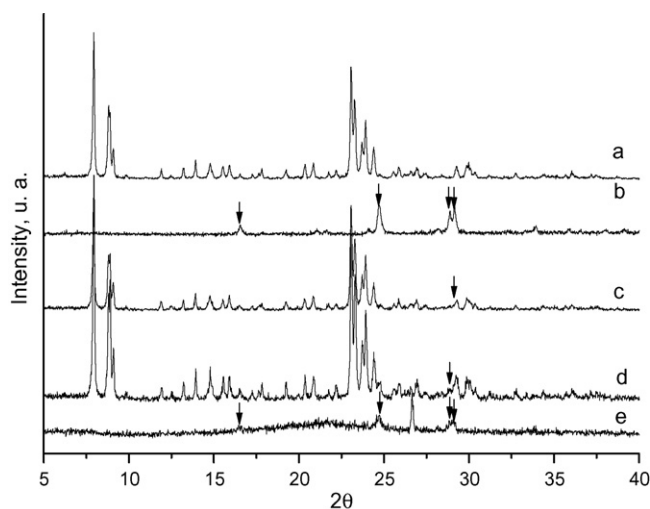


Fig. 2. X-ray diffraction pattern of: (a) ZSM-5, (b) CuV bulk, (c) CuVZSM-5(h), (d) CuVZSM-5(m), (e) CuVSiO<sub>2</sub>(m).

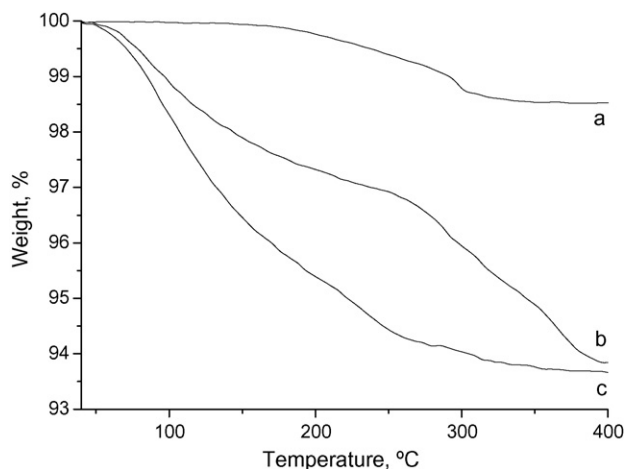
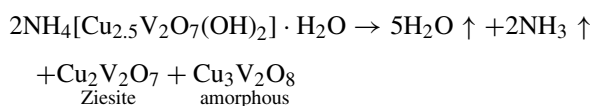


Fig. 3. TGA of supported catalysts: (a) CuVSiO<sub>2</sub>(m), (b) CuVZSM-5(h), (c) CuVZSM-5(m).

sor can be estimated as NH<sub>4</sub>[Cu<sub>2.5</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>]·H<sub>2</sub>O. From the identification of phases by X-ray diffraction and composition of the bulk catalyst, the following transformation at 320 °C can be proposed:



The thermogram of the supported catalysts is shown in Fig. 3. The weight loss observed with the SiO<sub>2</sub>-supported catalyst is attributed to volatile compounds released from the copper vanadate precursor. ZSM-5-supported catalyst has an additional weight loss, due to the release of water absorbed in the zeolite. The calcined ZSM-5 sample used to support copper vanadate had a water content of 5.5% and the copper vanadate precursor showed a weight loss of 10.9% at 322 °C and 11.6% at 400 °C. From the weight loss data observed at 400 °C with the supported catalysts, the amount of precursor in the catalyst was calculated and from these percentages

and the weight loss at 322 °C, the quantity of calcined copper vanadate was found (see Table 1). Both samples with zeolite have identical values for the total weight loss and the curves are practically coincident at 400 °C. However, the evolution of the curves is different, the sample prepared by mechanical mixture evidences a linear weight decrease until about 250 °C, while the hydrothermal sample shows an intermediate step, followed by a linear decrease that stabilizes at 400 °C. This difference of behaviour can be attributed to diffusion problems that at lower temperatures difficult the release of volatile compounds, because it is probable that some copper vanadate particles could be deposited in the pore mouth of ZSM-5 when the catalyst sample is hydrothermally treated. The deposition of metal particles inside the pores of the zeolite cannot be envisaged because the micropore volume measured by N<sub>2</sub> adsorption had not a significant reduction from the blank zeolite (0.15 cm<sup>3</sup> g<sup>-1</sup>) and samples with copper vanadate (0.13 cm<sup>3</sup> g<sup>-1</sup>).

### 3.3. UV–vis spectroscopy

The DR spectra in the UV region of the supported catalysts and copper vanadate catalyst are shown in Fig. 4 A and B. In this region, intense bands corresponding to ligand-to-metal charge transfer transitions are observed [18]. The bands that appear between 220 and 350 nm can be assigned to charge transfer transitions on tetrahedrally coordinated V<sup>5+</sup> ions [18,19]. This is in agreement with the crystal structure of copper vanadate phases present in the catalysts.

UV–vis absorption spectra reflect the electronic structure of valence bands in solids, but the broad nature of charge transfer features in the spectra of metal oxides makes it difficult to define the position of these bands from the energy at maximum absorption [20]. Band gap energies may be estimated by extrapolation to the energy axis of the linear portion of  $F(R)^2$  versus energy curves within the absorption edge of the charge transfer bands in solids [21]. The band gap energy obtained from the intense band (see Fig. 5) for bulk CuV is 2.56 eV, which

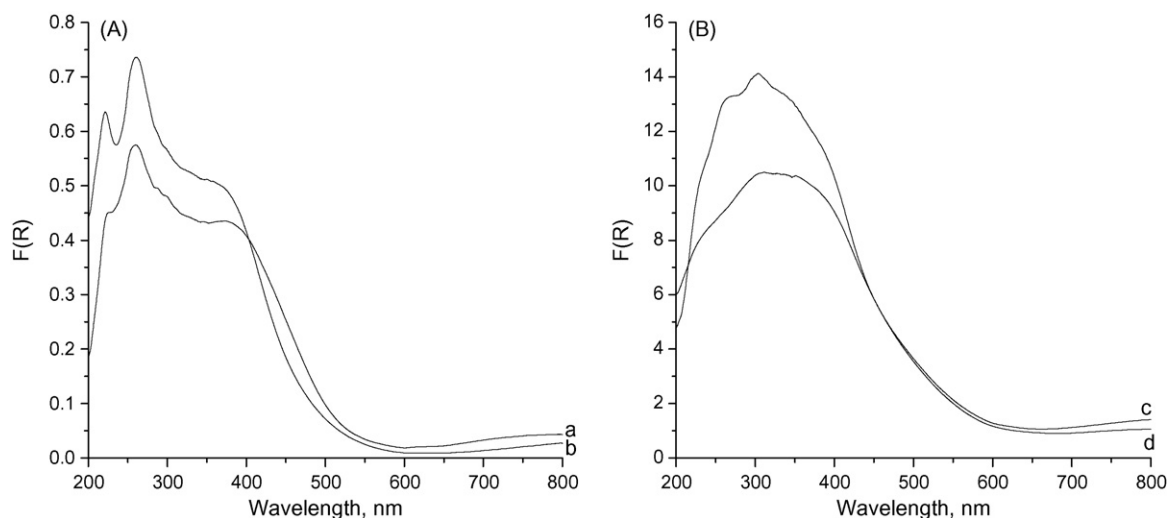


Fig. 4. Diffuse reflectance spectra in the UV range: (A-a) CuVZSM-5(m), (A-b) CuVZSM-5(h); (B-c) CuV bulk, (B-d) CuVSiO<sub>2</sub> (m).



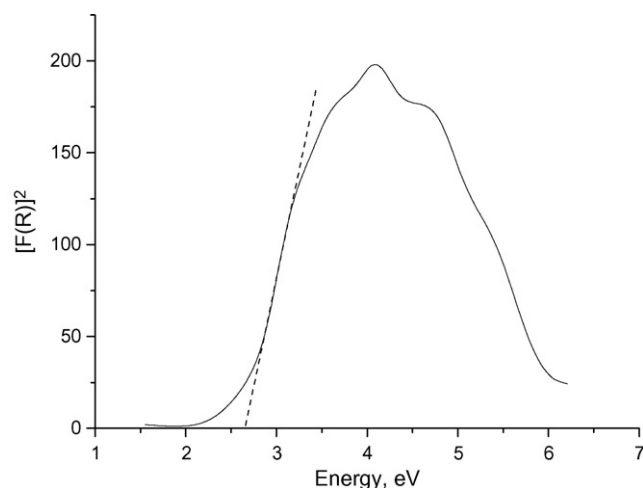


Fig. 5. Diffuse reflectance spectra in the UV range.  $[F(R)]^2$  vs. energy for CuV bulk.

is close to the value obtained for bulk  $V_2O_5$  (2.27), evidencing that we succeeded to detect absorption band energies which reflect  $O^{2-}$  to  $V^{5+}$  ligand-to-metal charge transfer transitions. Using the same method described above for bulk CuV, band gap energy values were obtained for each supported catalyst, as shown in Table 2. It is found that the catalyst having the highest value of band gap energy is CuVZSM-5(h) prepared by the hydrothermal method. There are some relationships that correlate band gap energies with particle size and dispersion [21] and it is known that when the particle size of a semiconductor decreases, the band gap between the valence and conduction bands increases [21]. In our case, the slight increase observed for the gap band energy seems to indicate that the copper vanadate is more dispersed in ZSM-5 when the hydrothermal method is used to incorporate the active phase. In fact the probability to have clusters or small particles is higher than in the other supports [22].

### 3.4. $H_2$ -temperature-programmed reduction

Fig. 6 shows the  $H_2$ -TPR profiles of the supported and bulk copper vanadates. The bulk catalyst has a complex profile with different reduction peaks corresponding to copper and vanadium species. This profile has been analysed based on the TPR profiles of  $V_2O_5$ , CuO and a mechanical mixture of oxides prepared with V and Cu contents similar to the composition of the catalysts and then calcined at  $550^\circ C$ . The results are reported on a previous work [17] that shows that copper oxide reduction occurs at about  $320^\circ C$  and vanadium pentoxide is reduced at higher temperature ( $600$ – $700^\circ C$ ). The oxide mixture evidences a more complex TPR profile emerging at intermediate temperatures and showing

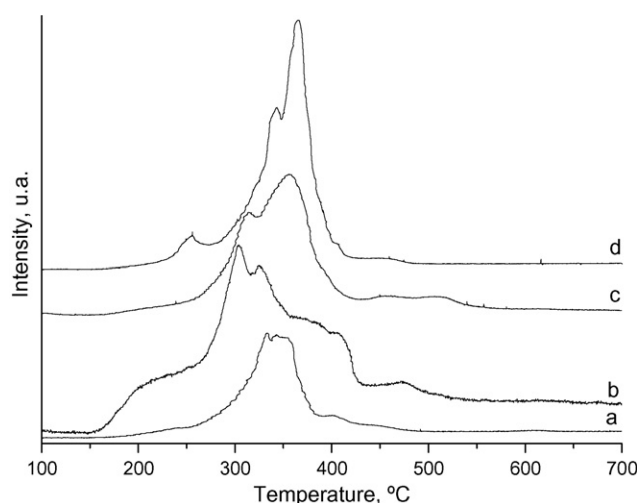


Fig. 6.  $H_2$ -TPR profile of CuV catalysts: (a) CuVSiO<sub>2</sub> (m), (b) CuVZSM-5(h), (c) CuVZSM-5(m), (d) CuV bulk.

that in that case copper is reduced at higher temperature and vanadium at lower temperatures.

All TPR profiles observed with the supported catalysts (Fig. 6) are complex and similar to the one of bulk catalyst. However, some differences in the temperature reduction and in the relative intensity of the peaks can be detected. For example, the catalyst supported on ZSM-5 using the hydrothermal method evidences a larger reduction peak that starts at lower temperature (at about  $170^\circ C$ ) and finishes at about  $420^\circ C$ . This large peak is composed by several components being the most intense placed in the temperature range from  $250$  to  $350^\circ C$  which, comparatively to the other catalyst profiles, is shifted to lower temperatures. Moreover, a large shoulder from  $170$  to  $250^\circ C$  is only observed on this TPR profile. These observations clearly indicate that the metal species hydrothermally supported on ZSM-5 are more easily reducible than the ones incorporated by mechanical mixture in both ZSM-5 and  $SiO_2$ . The peaks of TPR profile of this last support (curve a) show a smaller intensity and it is difficult to identify the several components corresponding to different metal species identified in the copper vanadate bulk catalyst. It means that during calcination of the precursor mechanically mixed with  $SiO_2$  some changes on the reducibility of the copper vanadate species occurred. On the contrary, the TPR profile of catalyst prepared by mechanical mixture of copper vanadate on ZSM-5 shows that in this case the reducibility of species is preserved and it occurs at slightly lower temperatures. These last observations indicate that during calcinations steps,  $SiO_2$  support interferes in the re-crystallization of the copper vanadate phase. The interference of ZSM-5 is negligible and the dispersion and accessibility of metal particles can be in the origin of the slight displacement of reduction peaks to lower temperatures. The influence of ZSM-5 support on dispersion of copper vanadate particles is clearly observed on the TPR profile of catalyst obtained by hydrothermal method (curve b) discussed above. This result is also in agreement with the adsorption edge energy (gap energy) of vanadate species that can be a sign of a reduction of metal particles sizes hydrothermally deposited on ZSM-5.

Table 2  
Band gap energy of catalysts

Sample	$V_2O_5$	CuVSiO <sub>2</sub> (m)	CuVZSM-5 (h)	CuVZSM-5 (m)	CuV bulk
$E$ (eV)	2.27	2.51	2.73	2.53	2.65

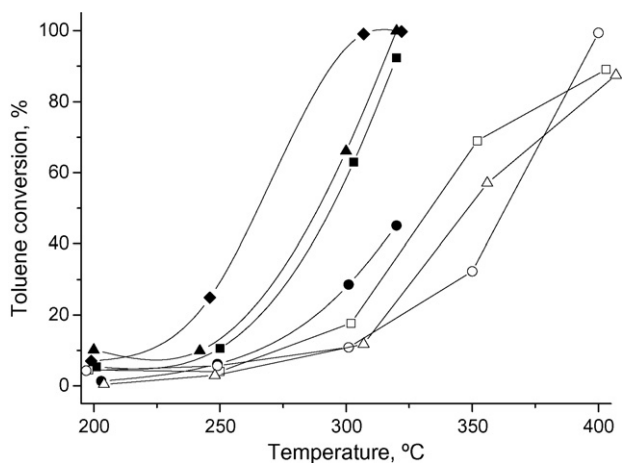


Fig. 7. Catalytic combustion of toluene. (●) CuVSiO<sub>2</sub>(m), (▲) CuVZSM-5(h), (■) CuVZSM-5(m), (◆) CuV bulk, (□) CuO, (○) V<sub>2</sub>O<sub>5</sub> and (△) CuO + V<sub>2</sub>O<sub>5</sub>. 800 ppm toluene in air; flow rate: 15 L h<sup>-1</sup>, catalyst weight: 300 mg.

### 3.5. Catalytic combustion of toluene

Catalytic measurements were carried-out with the ZSM-5 and SiO<sub>2</sub> supports and no conversion could be observed at the temperature range used in this work. The catalytic behaviour of copper vanadate (both bulk and supported) is shown in Figs. 7–9. The results observed with bulk catalysts based on CuO, V<sub>2</sub>O<sub>5</sub> and a mixture CuO/V<sub>2</sub>O<sub>5</sub> were also included in these figures. For the analysis of the figures it is important to point out that the catalytic tests were carried out using the same quantity of catalyst, which have not the same metal loading, or quantity of active sites. The CuV bulk sample and pure oxides CuO or V<sub>2</sub>O<sub>5</sub> have much more quantity of metal than the supported samples.

The total oxidation of toluene into CO<sub>2</sub> and H<sub>2</sub>O is the main reaction occurring in this type of catalysts, and apart from small amounts of CO that are detected with some catalysts, other secondary products were not found. From Fig. 7 that shows the toluene total conversion it is clear that there are great differences of activity between the several samples. Both CuV supported

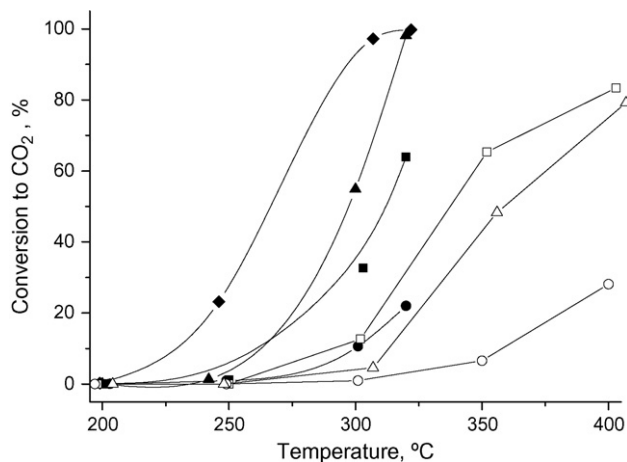


Fig. 8. Toluene conversion to CO<sub>2</sub>: (●) CuVSiO<sub>2</sub>(m), (▲) CuVZSM-5(h), (■) CuVZSM-5(m) and (◆) CuV bulk. 800 ppm toluene in air; flow rate: 15 L h<sup>-1</sup>, catalyst weight: 300 mg.

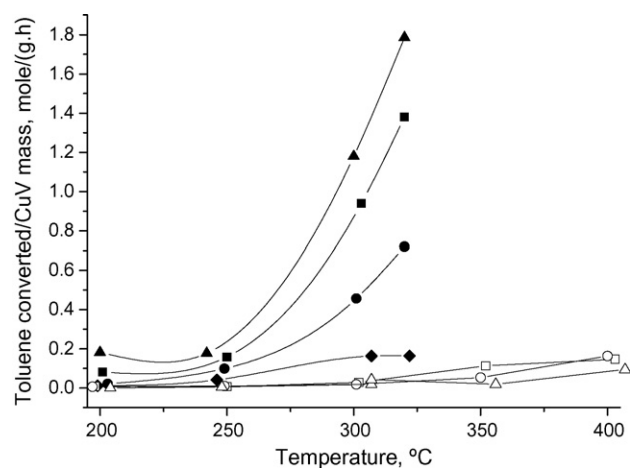


Fig. 9. Performance of the catalyst related to copper vanadate quantity: (●) CuVSiO<sub>2</sub>(m), (▲) CuVZSM-5(h), (■) CuVZSM-5(m), (◆) CuV bulk CuV bulk, (□) CuO, (○) V<sub>2</sub>O<sub>5</sub> and (△) CuO + V<sub>2</sub>O<sub>5</sub>. 800 ppm toluene in air; flow rate: 15 L h<sup>-1</sup>, catalyst weight: 300 mg.

ZSM5 samples with less metal loading and CuV bulk samples are able to convert 100% of toluene at identical temperature (about 320 °C), although the CuV bulk sample evidences higher conversions for lower temperatures. The main differences are found with the catalyst supported on SiO<sub>2</sub> that Exhibits 40% toluene conversion at 320 °C and the pure oxide bulk samples that are less active in all temperature range, being observed 100% conversion only for temperatures higher than 400 °C. Fig. 8 presents the conversion into CO<sub>2</sub> as a function of the temperature for all catalyst samples. It can be observed that at 320 °C the total toluene conversion into CO<sub>2</sub> is only reached with CuV-ZSM-5(h) and CuV bulk catalysts. The analysis of curves observed for pure oxide samples shows that V<sub>2</sub>O<sub>5</sub> is completely isolated and it is much less selective for CO<sub>2</sub>. The mechanical mixture of pure CuO and V<sub>2</sub>O<sub>5</sub> has catalytic performances more comparable to CuO, but in fact there is an enormous advantage to have copper and vanadium incorporated on the copper vanadate phase that we have been synthesizing and characterizing [15–17]. As it was pointed out before, the quantities of active phase are not the same in all the catalysts, so a better comparison can be made if toluene consumption is calculated on a basis of content of CuV phase, following the proportions reported on Table 1. The correction of results lead to the plots reported in Fig. 9 that, as it was expected, became the differences much more clear and show that the highest toluene conversions are observed with copper vanadate supported on ZSM-5 or even on SiO<sub>2</sub>, but the best performance is achieved with copper vanadate hydrothermally incorporated on ZSM-5. It can also be confirmed that CuV bulk phase is more active than pure copper oxide or vanadium pentoxide. These results also confirm that the dispersion of CuV phase in a support has great advantages, but correlating the catalytic behaviour with the TPR and UV–vis spectroscopy results, it seems that a better reducibility associated with higher gap energy provides an increase of activity. This could be associated to a better dispersion and small size of the catalytic particles. Moreover as it was seen, this is dependent on the type of support, being better for ZSM-5 than for SiO<sub>2</sub> support, which could

be associated with the role of the zeolite in the solid state reaction in order to transform, at 322 °C, the precursor into a catalyst.

#### 4. Conclusion

A new type  $\Phi_z$  copper vanadate precursor material was synthesised, with the formula  $\text{NH}_4[\text{Cu}_{2.5}\text{V}_2\text{O}_7(\text{OH})_2]\cdot\text{H}_2\text{O}$ . This material was supported into two different supports, ZSM-5 zeolite and amorphous  $\text{SiO}_2$ , by hydrothermal synthesis or mechanical mixture. All of the prepared catalysts were calcined under static air at 320 °C, which allowed us to obtain a copper vanadate phase (CuV), comprising two mixed oxides, one crystalline identified as Ziesite ( $\text{Cu}_2\text{V}_2\text{O}_7$ ) and according to our hypothesis, one amorphous ( $\text{Cu}_3\text{V}_2\text{O}_8$ ).

The best catalytic performance for total toluene oxidation was achieved with copper vanadate supported hydrothermally on ZSM-5. This behaviour was associated to a better reducibility and to a higher gap energy, which can be correlated to small particles and higher dispersion of metal phase in the ZSM-5 support.

The nature of the support seems to play an important role in the catalytic performance. Work is in progress to explore the support effects in these promising catalysts for VOCs elimination.

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