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Catalytic oxidation of volatile organic compounds with a new precursor type copper vanadate

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Abstract

Catalytic oxidation of toluene in low concentration (800 ppm) in air was carried out over catalysts prepared from a new copper vanadate phase calcined at different temperatures. The catalysts were composed of different crystalline phases, namely ziesite, fingerite, blossite and other copper vanadium oxides. The best catalytic performance was obtained with the material calcined at 320 °C (composed of ziesite phase and an amorphous copper vanadium oxide) that showed a light off temperature of 265 °C. H_2-TPR measurements indicated that the most active catalysts (calcined at 320 and 400 °C) are also the most easily reducible.

Keywords: Volatile organic compounds; Toluene combustion; Copper vanadate

1. Introduction

Volatile organic compounds (VOCs) are one of the main pollutants of the air. They include a large range of hydrocarbons with several functional groups, and they can be originated from different sources, such as chemical and petrochemical industries, plastic, food, paint, adhesive or coating manufacturing.

Adsorption is the method more commonly used to control VOCs in the air, generally over activated carbon. This method can provide the recovery of some of the compounds, but the process is very expensive at low concentrations of VOCs [1].

Thermal combustion has been implemented for the elimination of VOCs, but it requires high temperatures (higher than 800 °C) and it can lead to the production of compounds even more dangerous than the ones to be eliminated. Consequently, the catalytic combustion appears to be a very promising alternative for the elimination of VOCs, due to the energy saving that it can provide comparatively to thermal combustion.

In literature, a great number of studies about catalytic combustion of VOCs have been found, reporting the behaviour of catalysts based on noble and transition metals. Pt, Pd and Rh are generally supported on silica [2], alumina [3] and activated carbon [4,5]. This type of catalysts evidences high activities and selectivities at low temperature (lower than 200 °C), but they are very expensive and unstable in the presence of chloride compounds [6]. Transition metal oxides have been also intensively studied and successfully used in the catalytic combustion of hydrocarbons, by their low cost (comparatively to noble metals) and their stability. Usually, they are supported over porous oxides [6–9] or used as bulk catalysts without support [10,11]. Many results have been reported with different transition metals (Fe, Co, Ni, Cu, Zn, Mn, Ag, V, Cr, W, etc.), the copper-based being the ones that exhibited the lowest combustion temperatures [11–13]. Perovskites based on La, Sr and Mn also present very interesting catalytic behaviour and for example in the case of toluene combustion it is possible to reach the total conversion at 235 °C [11]. Exploring new materials with potential catalytic properties, Hoyos [14] synthesized a series of vanadates, belonging to the so-called Φ_z family. This structure is characterized by containing Brucite-type layers (with vacancies distributed), connected by pyrovanadate groups [15,16]. These lamellar materials have compensation cations and water molecules between the layers.

These materials, based on a system comprising Cu and V, can be examined as potential catalysts for catalytic combustion of VOCs because copper was found to be a very promising

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catalyst for the complete oxidation of aromatics [17,18] and vanadium oxide is one of the most active catalysts for a great variety of oxidation reactions [19]. In this work we used one of these new Φ_z type copper vanadates as precursor of bulk catalyst, and we evaluated the catalytic behaviour in toluene combustion. Toluene was selected as 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.

The precursor and the catalysts were characterized by powder X-ray diffraction (XRD), chemical analysis, thermogravimetry/differential scanning calorimetry (TG/DSC) and temperature-programmed reduction with hydrogen (H_2-TPR).

2. Experimental

2.1. Catalysts preparation

The precursor, a new copper vanadate, was prepared by hydrothermal method following the procedure of Hoyos [14]. The catalysts samples were obtained calcining the precursor at different temperatures. For the synthesis of the precursor, 1.5 g of V_2O_5 (Aldrich, 98%) were added to a solution previously prepared with 40 mL of distilled water and 4.9 mL of NH_4OH (Fluka, ~25%). Then, the suspension was homogenized for 45 min. Separately, 3.5 g of $CuCl_2 \cdot 2H_2O$ (Merck, 99%) were dissolved in 40 mL of distilled water. Copper solution was added to the vanadium mixture, forming a gel, which was magnetically agitated for 2 h. The final pH of the gel was 10 and its molar ratio was V_2O_5:2.5$CuCl_2$:4.7NH_4OH:538H_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.

The catalysts were obtained by calcination of the precursor at 320, 400, 500 and 600 °C in an oven, under static air and with a heating rate of 5 °C min^{-1}. These temperatures were chosen taking into account the results observed during the thermogravimetric analysis of the precursor.

2.2. Catalysts characterization

The vanadium composition was measured by atomic emission spectroscopy with plasma in PerkinElmer Optima 2000 V, the copper by atomic absorption in a PerkinElmer Analyst 300 and nitrogen by elemental analysis in Fisons Intruments EA 1108 CHNS equipment.

The precursor was analyzed by thermogravimetry with simultaneous differential scanning calorimetry in a Setaram TG–DSC 92 equipment, under a nitrogen flow of 25 mL min^{-1} and heating the sample at 5 °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. The surface area was calculated using the BET equation from N_2 adsorption isotherms.

Temperature-programmed reduction with hydrogen 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.

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 °C. The reactant mixture was supplied with a flow rate of 15 L h^{-1}. The feed and the reaction products were analyzed by an on-line gas chromatograph, equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) in series. The hydrocarbons and the carbon dioxide were analyzed with a Poraplot Q capillary column and carbon monoxide with a molecular sieve 5 A capillary column, both columns being connected in parallel.

The catalytic activity was evaluated in terms of toluene conversion and conversion to CO_2, in the temperature range between 100 °C and the temperature used to calcine the precursor and obtain the catalyst. At each reaction temperature, the conversions were analyzed after 1 h time-on-stream.

3. Results and discussion

The chemical analysis of the precursor and catalysts is shown in Table 1. The formula of precursor phase can be deduced from these data as $NH_4[Cu_{2.5}V_2O_7(OH)_2]\cdot H_2O$.

The TG/DSC plots reported in Fig. 1 show a first weight loss between 170 and 300 °C, that is associated with the simultaneous desorption of water and ammonia from the structure. This weight loss of about 12% agrees with the quantity of volatile

Table 1
Chemical composition of the precursor and catalysts calcined at different temperatures

Sample	Weight percentage			Molar ratio	
	Cu	V	N	Cu/V	N/V
Precursor	37	22	3.1	1.3	0.5
320 °C	41	24	–	1.4	–
400 °C	43	25	–	1.4	–
500 °C	43	25	–	1.4	–
600 °C	42	27	–	1.2	–

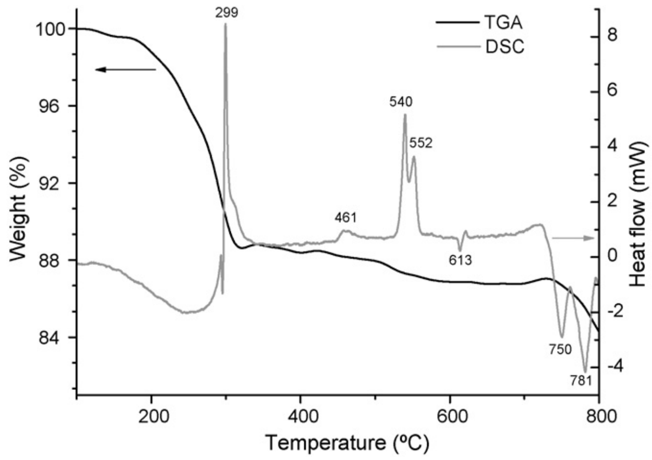

Fig. 1. TG and DSC profiles of the precursor.

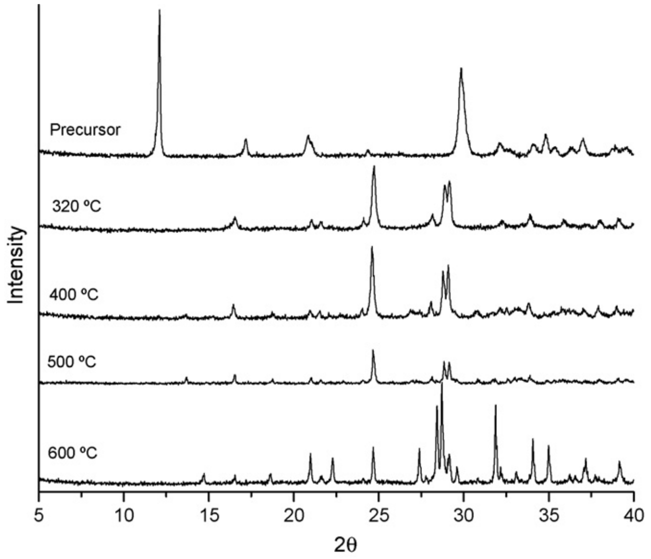

Fig. 2. XRD patterns of the precursor and catalysts calcined at different temperatures.

components that compose the structural formula shown above. Between 300 and 600 °C there is a slight weight loss (about 2%), probably due to the decomposition of some residual hydroxyl groups from amorphous phases that can be present together with the crystalline phases. In this temperature range some exothermic peaks are observed, indicating the occurrence of several phase changes. The endothermic peaks observed at temperatures higher than 700 °C can eventually be due to sublimation of a vanadium oxide.

Taking into account the phase transition that can occur with the increase of temperature, the precursor was calcined at 320, 400, 500 and 600 °C. The molar ratio Cu/V observed in both calcined solids and precursor (see Table 1) is practically the same, which means that in the temperature range of calcination (320–600 °C) only water, hydroxyls (under water form) and ammonium are volatilized and vanadium and copper are kept.

XRD patterns of the materials (precursor and calcined) are shown in Fig. 2. They confirm that the calcination of the precursor, at increasing temperature, leads to phase changes. At about 300 °C there is the formation of a new phase and in the temperature range 300–500 °C, the transitions are relatively small, but at 600 °C there is the formation of other phases. Tables 2 and 3 present the different crystalline phases identified (by formula and PDF number) for materials calcined at 320, 400, 500 and 600 °C. Comparing the results of chemical analysis with the composition of the crystalline phases present in the catalysts and performing a mass balance, it can be observed (Table 3) that the catalyst calcined at 320 °C contains a crystalline phase $Cu_2V_2O_7$ (ziesite) and an amorphous phase $Cu_3V_2O_8$. The simultaneous analysis of this table and the TG/DSC profiles of Fig. 1 can provide more details about structural changes occurring as a function of temperature. At 300 °C the precursor phase is transformed into ziesite (β-$Cu_2V_2O_7$) and when the temperature increases, the formation of the fingerite phase ($Cu_{11}O_2(VO_4)_6$) occurs. The peaks observed at 540 and 550 °C on the DSC profile correspond to a crystalline rearrangement, fingerite and ziesite being converted into three phases: the blossite (α-$Cu_2V_2O_7$) and two copper vanadium oxides ($Cu_3(VO_4)_2$) with different structures.

In some cases, like in the ziesite and blossite phases, the compounds have the same formula, but different structure. The same happens with the copper vanadium oxides, identified with

Table 2
Crystalline phases identified in the catalysts

	Name Ziesite	Fingerite	Blossite	Copper vanadium oxide	Copper vanadium oxide
Formula	$Cu_2V_2O_7$	$Cu_{11}O_2(VO_4)_6$	$Cu_2V_2O_7$	$Cu_3(VO_4)_2$	$Cu_3V_2O_8$
PDF	26-569	36-431	76-806	39-92	49-689

Table 3
Crystallite sizes (in nm) of the catalysts calcined at specific temperature and surface areas of the catalysts

	Phase name Ziesite	Fingerite	Blossite	Copper vanadium oxide	Copper vanadium oxide	Surface area ($m^2\ g^{-1}$)
320 °C	46.5	–	–	–	–	12
400 °C	67.8	55.2	–	–	–	8
500 °C	72.8	60.8	–	–	–	3
600 °C	51.2	–	14.8	136.8	76.0	1

the PDF number 39-92 and 49-689. Although the catalysts calcined at 400 and 500 °C present the same phases (ziesite and fingerite), there are structural differences because at 400 °C the fingerite is not completely crystalline.

In order to understand the structural transformations undergone by the precursor, we have tried to construct atomic models based on data extracted from inorganic crystal structure database. The structures models are shown in Fig. 3. Thus, it is possible to visualize the structure of the initial precursor (the atomic positions of an isomorphic zinc vanadate [22] were taken as a model, because the structure of the new copper vanadate is not yet solved) as a layered copper vanadate formed by copper octahedrons linked between them by pyrovanadates groups, containing water and ammonium molecules between the layers. When the precursor is calcined at 300 °C, water and ammonium molecules are released from the structure causing the collapse of the sheets and the rearrangement that leads to the formation of the ziesite phase and an other amorphous phase. The ziesite that was identified in all catalysts 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. Besides the ziesite, the samples calcined at 400 and 500 °C also contain the fingerite phase. This phase is composed of orthovanadates connected by three of their corners to copper polyhedrons in square planar coordination and the fourth corner is connected to a copper atom in square pyramidal coordination. The structure presents channels along the direction of *b* axis. At 600 °C the blossite phase and two copper vanadium oxides appear, one of them being isomorphic to McBirneyite phase. The blossite phase has pyrovanadate groups linked to copper in bipyramidal coordination and the structure presents channels in zig-zag along the *a* axis. The McBirneyite-type orthovanadate contains vanadium tetrahedrons attached by their corners to copper polyhedrons in square planar and square pyramidal coordination.

Table 3 presents the crystallite sizes determined for the several phases identified in the diffractograms. Crystallite sizes were calculated using the Scherrer formula that provides a correspondence with the full width at half maximum (FWHM). The FWHM was obtained for one peak from the XRD pattern in each sample. A model to simulate the scans of the phases present in the patterns was also used by means of the pseudo-Voigt mathematical function. These calculations were done using the DIFFRAC plus EVA software.

In general, the crystal size increases with the calcination temperature of the catalyst. For example, the ziesite phase that is present in all catalysts has crystallites of about 46 nm at 320 °C and 72.8 nm at 500 °C. At 600 °C, the crystal size of ziesite decreases, probably due to the transformation of ziesite into an other phase, namely the blossite phase. The two copper vanadium oxides also identified in the sample calcined at 600 °C have the largest crystal sizes.

Table 3 also shows the BET surface area determined for the four catalyst samples. The surface areas are very low for all

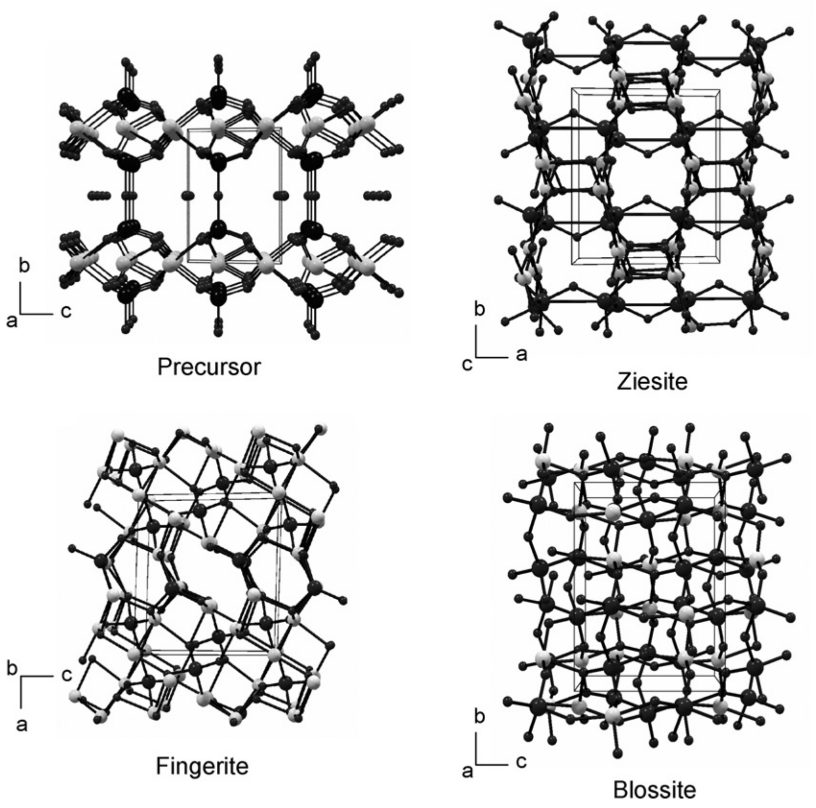

Fig. 3. Ball and stick view of structure of precursor and some phases present in the catalysts (drawn with powdercell [20], POVray [21]), with a silhouette of the unit cell. The large dark spheres represent vanadium atoms; the small dark spheres are oxygen atoms; the large light spheres are copper atoms and the water molecules appear as unconnected light spheres.

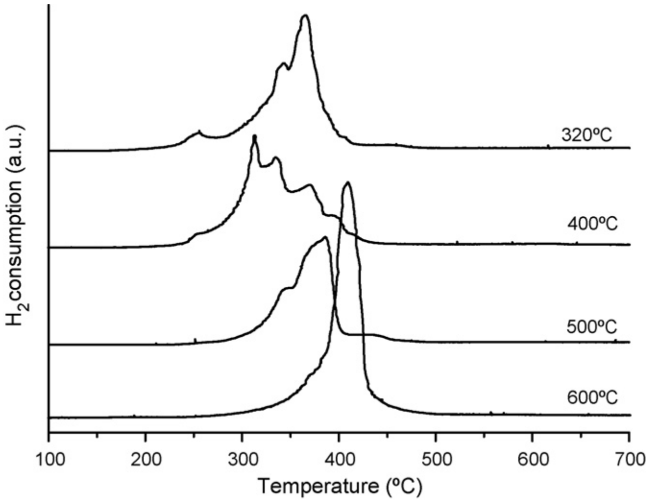

Fig. 4. H_2-TPR profiles of the catalysts calcined at different temperatures.

samples, but it is evident that the temperature increase leads to a reduction of the surface area. The decrease of surface area is in line with the particle sintering evidenced in samples calcined at high temperature.

Fig. 4 shows the H_2-TPR profiles obtained for catalysts calcined at different temperatures. Fig. 5 presents 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 °C. This last figure shows that copper oxide reduction occurs at about 320 °C, and vanadium pentoxide is reduced at higher temperature (peaks at 678 and 714 °C). The oxide mixture evidences a more complex TPR profile at intermediate temperatures, showing that, in this case, copper is reduced at higher temperature and vanadium at lower temperatures.

The literatures [12,23] also confirm that the reduction of CuO occurs at low temperature and in a single step $CuO \rightarrow Cu^0$. The cationic Cu species are usually reduced in two steps: $Cu^{2+} \rightarrow Cu^+$ that occur at low temperature and $Cu^+ \rightarrow Cu^0$ at higher temperatures. Wachs et al. [24] reported the reduction temperatures of V_2O_5 as ~675 °C for $V_2O_5 \rightarrow V_6O_{13}$, ~705 °C for $V_6O_{13} \rightarrow V_2O_4$ and ~780 °C for $V_2O_4 \rightarrow V_2O_3$. Other authors have assigned a reduction temperature of ~550 °C to isolated species of V in supported compounds [25,26] and reduction of V^{5+} in the framework of the catalyst at temperatures higher than 600 °C [27].

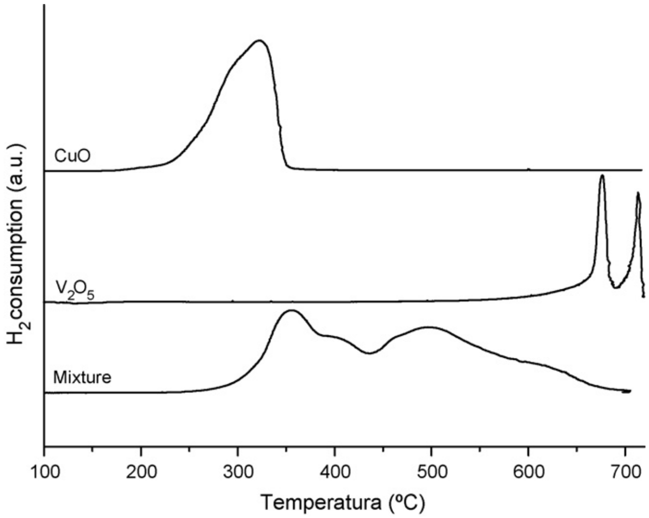

Fig. 5. H_2-TPR profiles of the CuO, V_2O_5 and the mixture CuO/V_2O_5 calcined at 550 °C.

Fig. 4 shows that, depending on the calcination temperature, the samples display profiles with several reduction peaks: low temperature peaks between 250 and 300 °C, medium temperature between 300 and 380 °C and high temperature between 380 and 460 °C. The lower temperature region of the reduction peaks plotted in Fig. 4 can be ascribed to reduction of copper oxide species and the higher temperature region to the reduction of V species, although it is hard to define a clear boundary between the two regions.

Comparing the temperature range for reduction of isolated copper and vanadium oxides (Fig. 5) and the temperature range of peaks corresponding to reduction of copper vanadate phases (Fig. 4), it is possible to conclude that, in this case, copper and vanadium species have particular environments and reducibilities. The main difference is observed for the reduction of vanadium, which occurs more easily than when it is alone and in the oxide form. The catalysts calcined at 320 and 400 °C show TPR profiles displaced to the lower temperatures, between 250 and 400 °C, contrarily to catalysts calcined at 500 and 600 °C, that require higher reduction temperatures, but all the metallic species are reduced in a smaller temperature range.

The performances of all catalysts obtained from precursor $NH_4[Cu_{2.5}V_2O_7(OH)_2]\cdot H_2O$ (Φ_z phase) by calcinations at 320, 400, 500 and 600 °C were evaluated for the total oxidation of toluene with air. The catalytic activity was evaluated in the temperature range between 100 °C and the temperature of calcination of each catalyst, since the phases that compose the several catalysts are metastable.

Fig. 6 shows the evolution of toluene conversion as a function of the temperature. The total oxidation of toluene into CO_2 and H_2O 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. It can be observed that all catalysts reached 100% toluene conversion, except for the sample calcined at 600 °C. The selectivity to CO_2 was 100% for the catalysts calcined at 320 and 400 °C. For the other two catalysts, at higher temperatures between 350 and 550 °C, the conversion of toluene to CO has also been detected in small quantities, with selectivities to CO lower than 17%. Fig. 7 that presents the evolution of light off temperature ($T_{50\%}$) as a function of the temperature of calcination of the catalysts clearly shows the increase of combustion temperature and light off temperature with the calcination temperature of the catalysts. Hua and coworkers [28] reported a similar behaviour. They prepared Mn and Zr mixed oxides with a method including calcination at 450, 600, 750 and 900 °C and concluded that at high temperatures the particles of manganese oxide were sinterized, causing the catalyst deactivation.

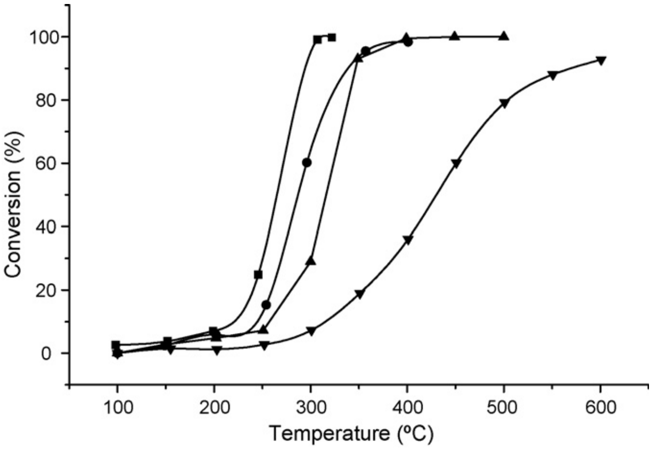

Fig. 6. Catalytic combustion of toluene with a new copper vanadate calcined at 320 °C (■), 400 °C (●), 500 °C (▲) and 600 °C (▼) (800 ppm toluene in air; flow rate: 15 L h^{-1}; catalyst weight: 300 mg).

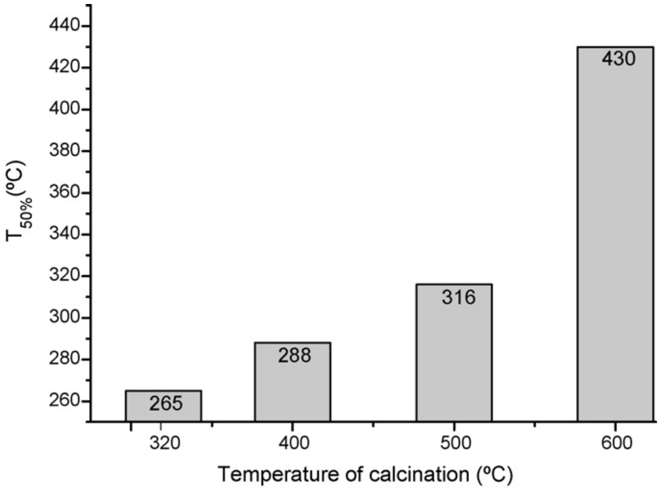

Fig. 7. Light off temperature as a function of the catalysts calcination temperature.

The copper vanadates used in this work, depending on the calcination temperature, are composed of different crystalline phases, which have different catalytic activity for toluene oxidation. The lowest light off temperature was reached with the catalyst calcined at 320 °C, composed mainly by the pyrovanadate ziesite (β-$Cu_2V_2O_7$) and the highest combustion temperature was obtained with the catalyst calcined at 600 °C, composed of two pyrovanadates (ziesite and blossite) and two orthovanadates ($Cu_3V_2O_8$). Therefore, it can be deduced that the presence of orthovanadates in the catalyst is not favourable for toluene combustion. On the other hand, taking into account the differences in crystallite sizes and textural properties observed with the different catalysts, it can be concluded that the best performances for toluene combustion are obtained with catalysts having smaller crystals and with the highest surface area.

In what metal reducibility concerns, the TPR measurements showed lower reduction temperatures for the most active catalysts calcined at 320 and 400 °C. As it was discussed before, the copper atoms are more easily reduced and are probably responsible for the catalytic activity in the toluene combustion.

The comparison of XRD patterns of catalysts before and after the reaction were identical, indicating that these materials are structurally stable for the temperature ranges required in the reaction.

Comparing our results for toluene combustion with those found in the literature with catalysts based on transition metals [6,8,10,26], it is possible to conclude that the catalyst calcined at 320 °C has a very good performance, because the majority of the published results have shown higher combustion temperatures than the observed with our catalyst ($T_{50\%}$ = 265 °C). For example, copper in oxide form supported on activated carbon fibres, when tested with 6 L h^{-1} of a feed containing 2000 ppm of toluene (1 g of catalyst), showed 80% of conversion at 300 °C [7]. Vanadium supported over HMS, tested under a space velocity of 38.4 h^{-1} and toluene concentration of 1000 ppm produced 90% of conversion at 550 °C [29].

We are aware that it is difficult to compare our results with those from the literature, because they are very dependent on the operating conditions used in the catalytic tests. But comparing our results for example with those observed with CuY zeolites [12] tested under the same conditions, we verify that those catalysts required a higher combustion temperature ($T_{50\%}$ = 340 °C) than the most active copper vanadate catalyst ($T_{50\%}$ = 265 °C).

4. Conclusions

A new material, type Φ_z copper vanadate with the chemical formula $NH_4[Cu_{2.5}V_2O_7(OH)_2]\cdot H_2O$ was synthesized and further calcined at 320, 400, 500 and 600 °C in order to obtain catalysts to be tested for the total oxidation of toluene. The calcined samples are composed of ziesite, fingerite, blossite and other copper vanadium oxides phases. In all the phases, the vanadium atoms are in octahedral coordination and the copper atoms have trigonal bipyramidal coordination in the case of pyrovanadates (like ziesite and blossite), but in the orthovanadates ($Cu_3(VO_4)_2$) the copper has square planar and square pyramidal coordination.

The composition of the samples depends on the calcination temperature and the structural differences evidenced by the various samples influence their catalytic behaviour in the total oxidation of toluene.

The catalyst calcined at 320 °C is composed of two mixed oxides, one crystalline identified as ziesite and one amorphous. It exhibited the best catalytic performances in toluene combustion, with a light off temperature of 265 °C. It appears that the reaction is disfavoured with the catalysts containing orthovanadate groups or isolated vanadium tetrahedrons that compose the phases present in the samples calcined at higher temperatures. Furthermore, H_2-TPR measurements indicated that the most active catalysts (calcined at 320 and 400 °C) are also the most easily reducible.

These results show that these copper vanadate precursors are promising catalysts for the oxidation of VOCs. Some improvements and studies are in progress using these materials.

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