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Additional Information

Influence of nanocavities formation on the catalytic performance of h-WO₃ type oxides

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Abstract

Vanadium free WO_3 and vanadium-containing $W_{0.92}V_{0.08}O_{3-x}$ oxides with the HTB structure have been prepared by hydrothermal synthesis. The addition of vanadium rises up the stability range of the hexagonal phase which became a stable polymorph up to 600º C. The structural characterization performed revealed the presence of a dense population of polyhedral nanocavities on the crystals surface distributed along particular crystallographic directions. Nanocavities are formed during the annealing process leading to catalyst activation and the process has been followed by TG/DTA-MS, HRTEM and HAADF STEM. The topotactic relationship between the as synthesized product and the desired heat-treated final product is proposed as the origin of the surface nanostructure. Samples calcined at different temperatures have been tested as ~~active~~ catalysts in the partial oxidation of H_2S and the results provide experimental evidence about the positive influence of the nanocavities in the catalytic activity of the materials. The process does not change the active centers of the catalysts which are mainly related to the hexagonal channels of the structure but the presence of cavities provides additional accessibility to the active plane of the structure and the consequence is a final enhancement of the catalytic performance. A broader treatment of the results achieved could spread the approach to different materials obtained by chemical reactions of solids leading to products with defined crystallographic orientation with respect to the original compound.

1. Introduction

Tungsten oxides are materials of huge interest due to its many known applications in electrochromic devices, [1] gas sensors[2] and photocatalysts.[3] WO_3 exhibits different structural modifications and among them hexagonal h-WO_3 (the so called HTB structure) is of considerable interest due to its open structure to be used as a selective host for intercalation and exchange chemistry.[4] WO_3 is also known as an effective catalyst in several acid catalyzed reactions[5]. As in other transition metal oxides, the suitable combination of W with other cations can be exploited to enhance WO_3 properties or even to extend them. In this sense, the substitution of W by Mo in h-WO_3 has been recently reported as a way to improve its NH_3-sensing properties.[6] Moreover, the selection of the adequate alkali cation additives during the hydrothermal process of synthesis, allows both the crystal morphology control as well as the structure stability.[7] In this sense, it has been proposed that the HTB framework cannot be maintained without traces of stabilizing ions or molecules in the hexagonal channels.

In the same way, adequately combined tungsten mixed metal oxides can exhibit interesting catalytic abilities. The existence of h-WO_3 with only residual occupation of the hexagonal tunnels[7] and, therefore, with accessible active acid sites, led to the idea of modifying the composition of the structural framework with the addition of vanadium[8] and transform the material into a bifunctional catalyst with acidic and redox properties simultaneously. The efficiency of these materials was tested in the transformation of glycerol to acrylic acid.[8] The acid activity for the dehydration to acrolein is given by the W-O bronze and the oxidizing function for the oxidation of acrolein to acrylic acid is given by the incorporated V ions. Therefore, structural and/or topological aspects may also play a crucial role in the catalytic behavior of W-based metal oxide bronzes. The spacial arrangement of important chemical sites is an essential aspect in any heterogeneous catalytic system but it is even more critical in a multifunctional system. Catalytic bifunctionality in (W,V)O_3 requires the two components to be adequately dispersed and accessible. Although a functional model for the W/V-HTB catalyst has not been established in the transformation reaction of glycerol to acrylic acid, the activity and selectivity of the two active sites have been

stated[8] and crystallinity is necessary possibly to prevent segregation of secondary phases and formation of unselective sites. In this sense, during the preparation process of these materials, the structural characterization performed revealed the presence of a dense population of polyhedral nanocavities distributed along particular crystallographic directions, on the crystals surface. Nanocavities are isolated nanoscale structures inside a solid, open to the surface and that do not connect together like nanopores. Nanocavities have been revealed as relevant constituents in photo-electrochemical systems,[9,10] but empty space has been also presented as a significant part of any nanostructured system where chemistry occurs[11] offering extra access to important active sites. In this scenario and provided the potential significance of our finding, we present here the results obtained in the investigation of the origin of this nanostructure. In addition, we provide experimental evidence about its influence in the catalytic activity of the material.

2. Experimental

2.1. Samples preparation

Vanadium free and vanadium-containing h-WO_3 samples were prepared by hydrothermal synthesis from aqueous solution of three different precursors: i) $Na_2WO_4 \cdot 2H_2O$; ii) $(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$; and iii) a mixture of $(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$ and NaCl.

In the synthesis of V-free samples (**W-O** series), oxalic acid was used as a reductor (with oxalic acid/W molar ratio of 0.07). Corresponding samples were named as (Na)**W-O**, (NH4)**W-O** and (Na/NH4)**W-O**, respectively. For the V-containing samples (**W/V-O** series), vanadyl sulphate was incorporated in the synthesis gel (with a V/W atomic ratio of 0.20). Corresponding samples were named as (Na)**W/V-O**, (NH4)**W/V-O** and (Na/NH4)**W/V-O**, respectively.

In all cases, the gels were loaded in Teflon-lined stainless-steel autoclaves and heated at 175ºC for 48h. The obtained solids were filtered off, washed and dried at 100ºC for 16 h. In order to obtain the final crystal phase, the obtained solids were calcined at 450º C (V-free materials) or 600º C (V-

containing materials) during 2 hours in a N_2 stream. The synthesis parameters are shown in Table 1.

2.2. Samples characterization

Powder X-ray diffraction patterns (XRD) were collected by using an Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic $CuK_{\alpha 1}$ source operating at 40 kV and 30 mA.

Thermogravimetric measurements were carried out on a Mettler-Toledo TGA/SDTA 851 instrument in the temperature range 20–600 ºC with 0.02 g samples (heating rate 10 ºC min^{-1} and air flow 100 ml min^{-1}). For the DTA / MS curves the measurements were performed in the 20–500 ºC temperature range (heating rate 10 ºC min^{-1}, 5% O_2/He, flow 25 ml min^{-1}). The relative masses corresponding to the main degradation compounds were analyzed with a mass spectrometer (Thermostar Balzers) coupled with the apparatus.

Samples for transmission electron microscopy (TEM) were ultrasonically dispersed in n-butanol and transferred to carbon coated copper grids. Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were carried out on a JEOL JEM3000F electron microscope (point resolution of 0.17 nm). Crystal by crystal XEDS microanalysis to determine the W/V cationic ratio was performed by using the same microscope equipped with an X-ray microanalysis ISIS 300 (Oxford Instruments) with a detector model LINK "Pentafet" (resolution 135 eV).

The microscope is equipped with a Scanning-TEM (STEM) unit and a high-angle annular dark-field (HAADF) detector. Z-contrast images were acquired using a collection angle of ~ 60 mrad. Electron energy-loss spectroscopy (EELS) data sets were acquired in STEM mode as line-scans with an ENFINA 1000 spectrometer (electron probe diameter of ~ 0.3 nm). The acquired low-loss spectra included the zero-loss peak and the plasmon peaks, so that sample thickness can be computed from each spectra.[12]

2.3. Catalytic tests

Catalytic tests for the partial oxidation of H_2S to sulfur were carried out in a fixed-bed quartz tubular flow reactor, in the 180–260 °C temperature range at atmospheric pressure. A total flow (130 mL min^{-1}) with H_2S/air/He molar ratio of 1.2/5.0/93.8 and a catalyst weight of 0.1 g were used. Analysis of reactants and reaction products was carried out online by using gas chromatography and two different chromatographic columns (Molecular Sieve 5A and Porapak T) .[13]

3. Results and Discussion

The preparation route of h-WO$_3$ has been described in the literature[14] as consisting in two steps: first, the hydrothermal treatment of an aqueous suspension of tungstic acid obtained from acid precipitation of sodium tungstate gives rise to the orthorhombic phase WO$_3$.1/3H$_2$O; then, its dehydration and transformation gives rise to h-WO$_3$ in the second step. Dehydration of the first product has been reported to occur prior to the reconstructive phase transition provided the close structural relationship between the two structures.[15,16]

Our initial interest concerning the preparation of hexagonal bronzes with empty tunnels, led us to use ammonium tungstate as precursor and the hydrothermal process gave rise to the orthorhombic WO$_3$.1/3H$_2$O as synthesis product. Further calcination, however, stabilized only the monoclinic m-WO$_3$ phase. The addition of a reducer such as oxalic acid was necessary to stabilize the hexagonal type lattice prior calcination in the materials prepared from ammonium tungstate and the h-WO$_3$ type phase formed turned into m-WO$_3$ at temperatures above 450° C (see figure S1 in Supporting Information).

The use of sodium tungstate does not improve the thermal stability of resulting solids. In this case, the addition of oxalic acid is also necessary to obtain a hexagonal type phase from the synthesis process. However, it cannot be fully stabilized and h- and m- phases coexist at 450° C (Figure S1 and Table 2). The use of a mixture of Na$^+$/NH$_4^+$ cations as templates allowed the stabilization of the HTB phase up to 450° C as well.

For the synthesis of the vanadium-containing samples, vanadyl sulfate was added to build up an h-WO_3 type framework in which tungsten is partially substituted for vanadium. Ammonium tungstate was used in addition to or in place of sodium tungstate as precursor. The presence of vanadium made not necessary the addition of oxalic acid to stabilize a hexagonal type phase. Reaction might follow a very similar pathway than for the vanadium free samples as deduced from the X-ray diffraction patterns of the as prepared materials (figure S2), and a hexagonal type phase was also directly obtained from the hydrothermal process. However, calcination of these samples, did allow the stabilization of h-$(W,V)O_3$ up to 600º C (Table 2 and Figure S2).

The powder X-ray diffraction of the as prepared samples did not show significant differences from the undoped sample to the vanadium-containing samples (figures S1 and S2). They all displayed diffraction patterns that could be interpreted on the basis of hexagonal tungsten type cells. They could be assigned directly to the hexagonal phase $Na_xWO_{3+x/2} \cdot zH_2O$, [17] very close to h-$WO_3$ (JCPDS Nº 33-1387) or to the hexagonal ammonium tungsten bronze $(NH_4)_{0.33-x}WO_{3-y}$ (JCPDS Nº 42-0452), depending on the precursor used in the synthesis procedure. For heat-treated samples leading to the HTB-type phase (Table 2), all the diffraction patterns were equally interpreted and the diffraction maxima could be indexed according to the unit cell of h-WO_3 (JCPDS Nº 33-1387, space group *P6/mmm*, cell parameters *a*= 0.7298 nm, *c*= 0.3899 nm).

The structural/microstructural aspects of the heat-treated samples were further studied in detail by Transmission Electron Microscopy. The analysis of the present crystal phases was in agreement with what we observed from powder X-ray diffraction data and heat-treated samples were constituted by h-WO_3 as single phase. In the V-containing samples, XEDS was used to determine the cationic ratio W/V on each crystal. The microanalysis performed showed that vanadium was homogeneously incorporated in all the crystals giving rise to an average stoichiometry $W_{0.92}V_{0.08}O_{3-x}$.

Crystals grew always in a preferential mode along the [001] direction giving rise to a characteristic rod like morphology with typical length and width values of

0.5-2 μm and 0.1-0.3 μm, respectively. Only vanadium doped samples prepared from sodium tungstate as precursor, showed plate-like crystal growth in the (001) plane, the crystals showing an average size between 1.5-2 μm. Vanadium containing samples prepared with the mixture of sodium and ammonium tungstate were formed by both type of crystals. It seems, therefore, that under the synthesis conditions employed, Na$^+$ cations act as templates for preferential growth in the *ab* plane.

Figure 1 shows the selected area electron diffraction (SAED) patterns corresponding to three different crystals of (W,V)O$_3$ in the (a) [100], (b) [1$\bar{1}$0] and (c) [001] zone axes. Although no evidence for doubling of the *c* axis was apparent in the X-ray diffraction patterns, (0 0 *l/2*) reciprocal lattice points are clearly observed (see figures 1(a) and 1(b)). According to this fact, diffraction maxima in the three projections are indexed on the basis of the hexagonal cell *P6$_3$/mcm,* a= 0.7298 nm, c= 0.7798 nm.[18] Octahedra tilting in the HTB-type compounds always seem to be observed and it has been previously reported as related to the doubled periodicity along *c.*[19,20] By rotating around their edges, the tilts of neighboring octahedra are equal but opposite, thus being the origin of the *c* parameter doubling although it does not modify the periodicity along *a.*

At this point it is important to mention that all the samples that retain the hexagonal type phase after the calcination treatment show very similar electron diffraction patterns, independently of the cation used as template.

Despite the hexagonal form is the only crystal phase observed by X-ray diffraction, electron diffraction patterns from our samples show always sharp elongation of diffraction maxima along [010] ([100]), [110] and equivalent reciprocal directions and diffraction patterns shown in figure 1 illustrate very well this fact. It appears both in crystals of samples prepared with alkali metals or with ammonium cations as templates. In addition, the electron diffraction pattern of some crystals in the [1$\bar{1}$0] projection presents a weak diffraction maximum doubling [111] and equivalent directions. It does not belong to the hexagonal phase as described but it can be assigned to the (101) maximum of the monoclinic phase m-WO$_3$ [21] to which the hexagonal form evolves when increasing temperature. [22,23] This is a reliable interpretation provided the metric

correspondence between the $[1\bar{1}0]_h$ - $[010]_m$ reciprocal projections and the similarity of d_{001} on both structures and will be discussed latter.

Figure 2 shows the high resolution electron micrographs of three different crystals of $(W,V)O_3$ in the (a) [100], (b)) $[1\bar{1}0]$ and (c) [001] projections. The image contrasts can be easily identified and correspond to the main directions of the HTB-type phase. In addition, areas with double periodicity along [001] can be distinguished (see figure 2b). We observe no additional contrast that could be related to the streaking observed in the diffraction patterns.

A remarkable property of these heat-treated materials concerns the crystals surface. A well disperse and dense distribution of polyhedral nanocavities is always observed in all the samples independently of the growth mode. From the careful observation of the images contrast on figure 2, the presence of the polyhedral cavities can be deduced, although they are better observed in slightly tilted orientation and in out of focus conditions. They appear as hollow (their nature will be further probed and explained) and well oriented polyhedra with faces parallel to [010] and [001] in the [100] projection (figure 2a), to [110] and [001] in the $[1\bar{1}0]$ projection (figure 2b) or parallel to $[1\bar{2}0]$ or [210] in the [001] projection (figure 2c).

Nanocavities present a regular size that ranges from 5 to 10 nm in both length and width. Pristine samples do not show cavities or irregular features in their surfaces. These nanovoids can be observed in the surface of the crystals from calcination temperature of 200 ºC. At this low temperature the surface of the crystals exhibit a porous sponge–like aspect (figure 3(a)) and the irregular pores turn into regular voids self-assembled along certain directions when increasing temperature up to 600 ºC (figure 3(b)).

We have further investigated the formation of the nanocavities provided the potential relevance it could have in the functional properties of the catalysts. Creating porosity in a solid catalyst may be a method to introduce new and controlled active sites. In this way, the creation of dense regular polyhedral nanocavities in TiO_2 by adequately choosing the synthesis precursor and the preparation method has been proved to be a simple and unique way to increase

the photoreactivity of TiO_2-anatase nanorods.[10,24] The suitable hydrothermal route produces $H_2Ti_3O_7$, whose dehydration gives rise to B-TiO_2 [24] or TiO_2-anatase [10] with dense nanocavities. The same kind of surface porosity has been recently observed in bassanite ($CaSO_4•0.5H_2O$) formed prior to gypsum precipitation;[25] in this case, bassanite is obtained from precipitation of $CaCl_2•2H_2O$ solution with Na_2SO_4 and nanocavities appear in the nanorods evolved from the growth and self-assembly of the initially formed bassanite nanocrystals.

The as-synthesized materials, i.e. $Na_x(W,V)O_3 . zH_2O$ and $(NH4)_{0.33-x}(W,V)O_{3-y}$, pass through different thermal transformations in the temperature range RT-600º C as shown by the corresponding thermogravimetric analysis (figure 4, patterns a-c). The structure of the hydrous oxide $Na_xWO_{3+x/2}.zH_2O$ has been reported to be very close to that of the high temperature HTB except by the fact that it contains Na^+ ions together with water molecules in the hexagonal tunnels.[26] The sodium ions are placed in the hexagonal windows and the water molecules are disordered along the z axis in order to maintain adequate Na-O distances. In addition to water molecules, oxygen anions and hydroxyl groups may also be present in these tunnel positions.

The low temperature (25 - 600º C) thermal transformations of $Na_xWO_{3+x/2}.zH_2O$ have been recently investigated [27] by means of thermogravimetric (TG/DTA), diffuse reflectance infrared (DRIFT) and ^{23}Na MAS NMR spectroscopic studies. Thermogravimetric analysis showed a progressive weight loss from room temperature to 300º C. The ^{23}Na MAS NMR spectrum of the hydrated product show three different Na species, the anhydrous Na placed at the center of the hexagonal planar site and two other species attributed to Na in the tunnel windows with different degree of oxo-coordination with water molecules along the tunnel direction. Heating at 100º C mainly produces tunnel dehydration but at 200º C the first structural transformation occurs and Na is distributed between the planar hexagonal positions and a new position which is in the center of the cavity between two hexagonal windows. All Na is essentially anhydrous but TG and DRIFT results show that the system remains partially hydrated at this temperature. Authors claimed that sodium rearrangement in the tunnels forces the residual water content into pocketed and regionalized

occlusions and it is not distributed throughout the tunnels. After heating at 300⁰ C, the entire system undergoes the transformation, with all the Na inside the tunnels.

The decomposition sequence of the hexagonal ammonium tungsten bronze $(NH_4)_{0.33-x}WO_{3-y}$ has been analyzed in detail by simultaneous TG/DTG/DTA and ^1H MAS NMR spectroscopy.[4a] It was observed that ammonium left the structure in three overlapping steps between 250 and 500⁰ C Authors postulate the existence of two different NH_4^+ species, the first being those ions bonded the weakest and closer to the surface which evolve together with water up to 200-250⁰ C. Around this temperature and up to 500⁰C, NH_4^+ ions located in the hexagonal tunnels of the structure are eliminated. They considered the existence of an intermediate species too but its origin was not clear.

The thermogravimetric analysis of the Na-containing samples is shown in figure 4a. There is a broad endothermic peak at about 230 – 250⁰ C on each thermogram which corresponds to a net weight loss of ~ 2.5–2.7%. This information could be in agreement with the observations of Griffith[4c] and Luca[27] and with the fact that it is about 200⁰ C when the first structural transformation associated with the water loss occurs. The vanadium free sample shows in addition an endothermic peak at ~ 80⁰ C which can be assigned to the first water evolution. This is not observed in the V-containing sample where the plate like morphology associated to preferential growth on the *ab* plane makes the length of the tunnels significantly shorter.

The thermogravimetric analysis of the NH_4^+-containing samples is shown in figure 4b. The thermal decomposition follows a very similar sequence in both cases and two overlapping steps are visible, the first one from room temperature to 200-250⁰ C and the second one from this temperature to ~500⁰ C. There are no significant differences between the samples with or without vanadium and in addition to the endothermic peak at 90⁰ C, two other broad endothermic peaks partially overlapped are observed between 200 and 500⁰ C. The thermal analysis of Na^+/NH_4^+-containing samples (figure 4c) presents strong similarity with those containing only NH_4^+. The same features as above

are observable and the weight loss takes place within the same temperature interval.

From all this information, we can highlight two important facts. First, one can find a strong parallelism between the main features of the thermal analysis of our samples and the information reported in the literature for the $Na_xWO_{3+x/2}.zH_2O$ and $(NH_4)_{0.33-x}WO_{3-y}$ materials which, indirectly, is telling us about the presence of different Na^+ and NH_4^+ species, as mentioned. In addition, it is a common fact that the first step in the weight loss takes place at a temperature about 200° C (figure 4a), and it is around this temperature when tunnels start to empty and former structures begin to transform into the hexagonal bronze. It is precisely at this temperature when nanocavities appear on the surface of the crystals. This is consistent with the fact that pristine samples do not show cavities or irregular features in their surfaces.

The mechanism by which the nanocavities are formed in TiO_2 has been explained by Han et al.[10] by using the "anti-crystal growth" model, as previously mentioned. There is certain degree of topotaxy between $H_2Ti_3O_7$ and TiO_2-anatase and *d* spacing of (001) and (010) planes are very similar in both structures. However, the unit cell of TiO_2 is much denser and the evaporation of water leaves empty space which, because of the topotactic relationship, occurs in certain energetically favored directions. Cavities are treated as empty nano-polyhedra, that is, a second phase which nucleates after dehydration for phase reconstruction and topotaxy favors it. In our case, both $Na_x(W,V)O_3.zH_2O$ and $(NH_4)_{0.33-x}(W,V)O_{3-y}$ present structures which are closely related to h-WO_3. When heating, water molecules leave their tunnel positions thus leaving the crystal and sodium atoms are redistributed, modifying their position. In the same sense, NH_4^+ ions are eliminated from the hexagonal tunnels. As a result, crystal shrinkage occurs and reconstructive phase transformation takes place through the formation of the highly topotactic final product (h-WO_3 / h-$(W,V)O_3$ phase) together with nuclei of a secondary phase, as cavities can be considered, self-assembled along certain preferential crystallographic directions which are common with those of the starting phase.

Confirmation that crystals correspond to nanovoid-structured materials comes from the characterization performed by means of HAADF STEM. Since this detector uses the electrons scattered at high angles (i.e., Rutherford scattering) for image formation, there is no phase contribution, the obtained images are very sensitive to the atomic number Z (Z-contrast imaging) [28] and, therefore, to the crystal thickness. Under these conditions, nanocavities are observed as dark areas in the images (see figure 3). EELS analysis from spectra across the dark regions provide semiquantitative information about depth of the cavities. The analysis performed does not reveal the presence of other elements than W, V and O in the crystals or in the cavities and there is no chemical segregation associated with the contrasts observed. Figure 5 shows the high magnification Z-contrast images of two different crystals, (a) a rod-like crystal of the (NH_4^+)**W/V-O** sample and (b) a plate-like crystal of the (Na)**W/V-O** sample. The position of the EELS line-scans is indicated by the drawn lines and the profiles across the lines show the decrease in thickness in the corresponding dark areas. The measured depth is always around 10-15 nm.

The hexagonal form of WO_3, h-WO_3, has always been referred in the literature as a metastable phase. [22, 23] However, a recent investigation on the formation of h-WO_3 from hexagonal ammonium tungsten bronze provided evidence about the structural framework collapse when NH_4^+ is completely released from the structure.[4a] Authors propose that the structure of h-WO_3 cannot be maintained without traces of stabilizing ions or molecules in the hexagonal channels. Based in their thermoanalytical and solid state studies, they found a parallelism between the complete elimination of NH_4^+ and the collapse of h-WO_3 and its transformation into m-WO_3. In our samples, both ammonium and/or alkali metals have played the role of structure directors during the synthesis procedure. After NH_4^+ evolution, the V-free material is transformed into m-WO_3. The evolved gas analytical curves displayed on figure S3 (Supporting Information), show the release of NH_3 beginning at $\sim 200^\circ$ C for the W-O sample and above 300° C for the W/V-O material. In addition, water is eliminated in two steps, the first one at about 250° C is common in both curves but the second one occurs at 400° C for the V-free sample and at 500° C for the V-containing sample. Water eliminated at these high temperatures is explained

as combustion product of the as-released NH_4^+ and the higher temperature in V-containing sample can be related to the fact that ammonium is more tightly retained in this framework. In fact, the V-containing sample retains the h-WO_3 form up to 600º C (see figure S2). In the Na- containing samples, heat-treatment leads to the release of water but sodium remains in the structure. However, the hexagonal phase is not retained in the V-free sample. Therefore, it seems that it is the addition of vanadium the factor that rises up the previously reported stability range of the hexagonal phase which became a stable polymorph at 600º C.

In the study of Figlarz, [22] the transformation of h-WO_3 to the stable monoclinic polymorph is reported to occur at 490º C in crystals grown in the $(100)_h$ planes and slightly above 400º C for crystals grown on the $(001)_h$ plane. Authors propose the transformation takes place on a topotactic way providing the structural similarity between the (100) planes of the monoclinic phase and alternate (200) planes of the hexagonal structure. Thus, the monoclinic form begins to grow in the (200) planes (or equivalent orientations). The schematic representation of Figure 6(a) illustrates the intergrowth of both structures in two different projections. The streaking of the diffraction maxima we have observed along [100] and [110] and equivalent directions is indicative of certain degree of disorder along these directions. In addition, the weak extra diffraction maximum doubling [111] in some crystals indicates that a structural transformation is taking place. Both facts could be easily interpreted if we assume that around the calcination temperature of 600º C, the hexagonal form begins the transition to the monoclinic polymorph. At the early stages of the transformation disorder occurs in a short range and, therefore, its origin is not clearly distinguished from the image contrast. As it goes on, regions of the new phase become apparent. Figure 6(b) shows a crystal oriented in the $[100]_h$ projection. The change of contrast in the crystal edge corresponds to the transformation to the monoclinic form in the [010] projection. The similarity between d_{001} for the two structures provides a good basis for the intergrowth of both crystal phases. The corresponding Fourier Transforms of each area have been included to illustrate the origin of the diverse diffraction effects.

At this point we should emphasize that cavities are not responsible for the streaking observed, as deduced from the careful processing of the image contrast in the micrographs areas.

In order to determine the possible influence of the surface microstructure on the catalytic properties of these materials, catalytic tests have been performed on (NH_4)**W/V-O** pristine sample and the corresponding calcined samples after treatments in N_2 at 250, 400 or 600º C, for comparison. Figure 7 shows the variation of the specific activity (in $mmolH_2S$ m^{-2}) with the reaction temperature achieved during the partial oxidation of H_2S on heat-treated samples. This reaction has been chosen provided its relevance from an environmental point of view and because of the fact that it takes place at moderate temperatures (< 250º C). This ensures that there won´t be any modification, as an effect of temperature, on the surface nanostructure as a result of the catalytic process and allows comparing the results obtained on the materials previously calcined at different temperatures. In all cases, the selectivity to sulfur was higher than 98%. Although similar catalytic activity for both the pristine sample and the sample heat-treated at 250ºC is observed, it increases when increasing the calcination temperature. As previously mentioned, once the water and/or ammonium molecules depart from the crystals thus leaving empty spaces, the structure begins to rearrange progressively when rising temperature and the empty spaces became self-assembled nanocavities along certain crystallographic directions. The process does not change the active centers of the catalysts which are mainly related to the hexagonal channels of the structure [29,4c]. However, since there is preferential growth along the [001] direction most of the crystals area is oriented perpendicular to the (001) plane. The presence of cavities provides additional accessibility to the active plane of the structure and the consequence is a final enhancement of the catalytic performance for the highest calcination temperature (figure 6c).

In summary, the hydrothermal route followed to prepare h-$(W,V)O_3$ catalyst materials has led to the formation of a dense distribution of self-organized nanocavities on the crystals surface. The topotactic relationship between the as synthesized product and the desired heat-treated final product is proposed as the origin of the surface microstructure, after evolution of water and/or

ammonium species. Explained in this way, it bares strong similarity with the origin of polyhedral cavities recently observed in TiO_2 crystals where their presence improves the photoreactivity. A parallelism between the formation of nanocavities and catalytic activity in our case is inferred from the investigations performed probably by improving the accessibility to the active sites.

A broader treatment of the results achieved could spread the approach to different materials obtained by chemical reactions of solids leading to products with defined crystallographic orientation with respect to the original crystal by exchanging components with the surroundings. Mild synthesis conditions provided by the hydrothermal processes are probably necessary and different degrees of conservation of structural elements can occur as exemplified by TiO_2 that retains certain crystallographic relationships with its precursor[10] or by $(W,V)O_3$ where there exists a close structural relationship by keeping the three-dimensional skeleton. The incorporation of this approach to materials displaying different abilities involves improving their chemical/physical final properties.

Acknowledgements

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