Structure–Reactivity Correlations in Vanadium-Containing Catalysts for One-Pot Glycerol Oxidehydration to Acrylic Acid

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Multi-element crystalline and pseudo-crystalline oxides as efficient catalysts for the direct transformation of glycerol into acrylic acid

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Introduction

Despite the 2008-2009 global recession, world energy consumption is foreseen to grow with an outstanding 56 percent increase in 2040 and in order to satisfy this demand renewable fuels, together with conventional sources, will play an important role.[1] In this regard, since early ‘90s, biodiesel has been addressed by many Countries as one of the most favourable choices;[2-4] indeed, in spite of unclear ecological and ethic aspects related to its production,[5] large amount of money has been invested in the biodiesel sector and current figures are foreseen to double within 2020.[6,7] Therefore, hand-in-hand with the biodiesel growth, co-produced glycerol represents an abundant bio-based building block for the synthesis of a wide range of chemicals and a crucial economic opportunity to valorise the biofuel production chain.

Amongst the various options for glycerol upgrading, the dehydration process to acrolein is one of the most debated in literature since this aldehyde is the intermediate molecule for the production of important chemicals such as DL-methionine and acrylic acid.[6,8-10] In this regard, the one-pot synthesis of acrylic acid from glycerol theoretically allows avoiding the production of intermediate acrolein, thus restricting toxicity concerns related to this aldehyde and simplifying reactor design and heat exchange. Moreover, it would represent a more sustainable route to (at least partially) substitute the current production of acrylic acid from propylene, the latter being obtained from the cracking of nafta. At the same time it would also allow to smooth the influence of the increasing propylene price [11] on the final cost of the acid monomer. So far, two different approaches have been taken into consideration for the one-pot synthesis: (i) the utilization of a single multifunctional catalyst with both acid and redox properties[12-19] or (ii) coupling of two catalysts (dehydrating and oxidizing) as two in-series fixed-beds in a single reactor.[20-22] The latter approach is generally accepted to lead to higher yields into acrylic acid even though serious limitations can derive from being forced to use the same reaction conditions for both catalytic beds. Otherwise, the use of more complicated technologies to overcome this issue (e.g. inter-stage heat exchange) could severely affect the economic feasibility of the process and its competitiveness to the current propylene-based one. Nevertheless, the multifunctional catalyst approach is very demanding from the catalyst design standpoint, since only fine tuning of acid and redox properties of the material allows obtaining noteworthy yields into the acid monomer. Indeed, few multifunctional materials have been so far demonstrated to be effective catalysts for the direct transformation of glycerol into acrylic acid, i.e. $FeVO_4/Fe_2O_3$,[12] Mo-V-O, Mo-V-Te-Nb-O, W-V-(Nb)-O[13-18] and V-impregnated zeolites.[19] In this paper we report a new class of catalysts that shows high yields into acrylic acid, up to 51%. The introduction of Mo in a W-V mixed oxides create not only changes in the catalyst structure but also leads to a multifunctional material with both Brϕnsted acid and redox sites, as well as stable oxidizing properties on a wide range of temperature. The W-Mo-V catalysts presented here are revealed to be complex oxides constituted by a hexagonal bronze WO_x type phase and/or a pseudo-crystalline phase. We also demonstrate that the combination of the three elements is fundamental in order to optimize the glycerol oxidation to acrylic acid.

Results and Discussion

1. Physical-chemical properties

In order to study the influence of tungsten, molybdenum and vanadium on both the catalytic performance and the materials structure, bi-component W-Mo and tri-component W-Mo-V oxides catalysts were synthesized.

Figure 1 shows the XRD patterns of catalysts prepared by heat-treatment at 600°C in nitrogen; for the tri-component systems with low molybdenum contents (samples WMoV-1 and WMoV-2, patterns a and b) X-ray diffraction maxima can be assigned to a hexagonal tungsten bronze (HTB) type phase. Interestingly, crystallinity is considerably improved for the sample containing higher vanadium amount (WMoV-2), giving emphasis to the conclusion formerly drawn by our group that highlights how vanadium has a stabilizing effect on the HTB structure.[14] By keeping the W/V ratio and increasing the molybdenum amount (i.e. WMoV-3 and WMoV-4), diffraction patterns are dominated by two diffraction maxima at around 22° and 46° 2θ, while broad diffraction maxima appear at 2θ ~ 27°, 32°, 50° and 55° (Figure 1, patterns c and d). These patterns are similar to those reported for Mo- and W-based

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mixed oxides by Murayama et al..[23] According to these authors, samples with higher molybdenum content are characterized by two peaks at 2θ equals to 22° and 46° which can be attributed to the (0 0 1) and (0 0 2) planes of a bronze type frame, suggesting that these materials have a layer-type crystal structure. In fact, these diffraction maxima can correspond to the (1 0 0) and (2 0 0) d-spacing of any structure based on the corner sharing octahedral ReO_3-like framework with a basic cell parameter of about 3.8 Å. When considering the whole set of diffraction maxima, although ill-defined, they are all compatible with the well-known orthorhombic tungsten bronze $Cs_xNb_{2.54}W_{2.46}O_{14}$[24] or the so-called Mo-V-Te-Nb-O M1-phase.[25] Provided the unclear identity of the present crystal phases, the samples were further investigated by electron diffraction and high resolution electron microscopy. In agreement with XRD data, the tri-component samples with low Mo-content, i.e. WMoV-1 and WMoV-2, are constituted by crystals of the hexagonal phase, with bigger crystallites in sample WMoV-2 (average size > 100 nm vs. 50-100 nm for WMoV-1)). For high Mo content (i.e. WMoV-3 and WMoV-4), the HTB phase is not stabilized and samples are formed by smaller crystallites, i.e. 10-50 nm, as shown by electron diffraction ring pattern for the WMoV-3 sample (Figure 2a). The corresponding high resolution image (figure 2b) shows a group of crystals in which lattice fringes are observed at d-spacing of about 3.8 Å. Image contrasts illustrates very well the ill-defined periodicity along the perpendicular direction and disordered packing of structural planes. This low resolved structural arrangement is consistent with the previous interpretation of the corresponding XRD pattern. In the absence of vanadium, XRD patterns show strong similarity with those of samples containing vanadium, the W/Mo-ratio playing a pivotal role in stabilizing the HTB-type phase. Figure 2c shows a rod-like crystal of the WMo-2 sample. Lattice planes equally spaced at ~3.8 Å can be observed as well as disordered contrast along the perpendicular direction;

moreover the image contrast is very similar to that on figure 2b, although the average crystal size is above 100 nm. In order to facilitate the formation of well crystallized phases and as a help in the elucidation of the nature of these materials, the same catalysts precursors were heat-treated in nitrogen at 800°C - see experimental section-. XRD patterns of samples heat-treated at 800°C (i.e. WMoV-1[800], WMoV-3[800] and WMo-2[800]) are also shown in Figure 1 (patterns g, h and i). The three patterns reveal the formation of a monoclinic WO_3-type phase (m-WO_3), besides a certain amount of Mo_5O_{14}-type phase in the samples containing vanadium (as shown by peaks at ca. 7.7º and 8.4º 2θ). The WMoV-3[800] sample is formed by m-WO_3 type phase as major component, which according to the electron microscopy study (figure S1(a)) do not contain vanadium, the average atomic composition being $W_{0.7}Mo_{0.3}O_3$. Interestingly, vanadium is segregated into the M_5O_{14}-type phase crystals which constitute the minor component of the sample and their atomic average composition is $(W_{0.64}Mo_{0.3}V_{0.03})_5O_{14}$ (figure S1(b)).

All the above results are consistent with the idea that catalysts heat-treated at 600°C are constituted by a matrix built up of corner sharing MO_6 octahedra and distributed in orderly stacked crystal planes (d ~ 3.8 Å). Inside the planes, further structural reconstruction is needed to achieve a particular structural type, as demonstrated by the ill-defined diffraction maxima and the disordered contrast of the high resolution images. Indeed, being the h-WO_x phase metastable, very specific composition/temperature conditions are required for its formation.[14,26,27] In this sense, previous structural investigations on the $W_xMo_{1-x}O_3$ system have shown that in the $0.25 \leq x \leq 0.70$ composition range, materials adopt the ξ-type phase, very similar to that of m-WO_3 although the unit cell presents higher distortion, with random distribution of the metal atoms in the same space group $P2_1/n$.[28] The phase appears at room temperature and for $x < 0.5$; rising T between 100 and 420º C, it transforms into γ-WO_3, which is equivalent to pure m-WO_3. Our results show, however, that the monoclinic phase cannot be stabilized below ~800°C.

FTIR spectra were recorded for W-Mo and W-Mo-V catalysts (Figure 3). Both V-free and V-containing samples are similar. A broad band centred between 814 and 830 cm^{-1} can be assigned to W–O–W(Mo) stretching, whereas band at 724 should be related to W–O–V; bands at 643 and 576 cm^{-1} may be associated to a W–O–W and W–O–V rocking vibration and to Mo-O-X (X= W or V).[29,30] Therefore, strong similarity between spectra is consistent with the above structural description where all the catalysts have a more or less regular distribution of corners sharing octahedra in the HTB- or pseudo-crystalline structure given the M-O-M vibrations observed.

The specific surface area for all the catalysts is shown in Table 1; the higher vanadium content in samples with the HTB-type structure (WMoV-1 and WMoV-2) the lower BET surface area, as a consequence of its higher crystallinity and bigger average crystal size, in agreement with our previous results on WV catalysts.[14] For samples containing the pseudo-crystalline phase (WMoV-1 vs. WMoV-3 or WMoV-2 vs. WMoV-4), the higher molybdenum content allows obtaining a significant increment of specific surface area, the effect being more relevant when vanadium content is higher.

A similar comparison can be done when characterizing the acid sites (see Table 1). The addition of molybdenum leads to a remarkable decrease in the overall acidity (see WMo-1 and WMo-2), both on mass and surface area basis; but Brϕnsted acidity increases. Similar trend is displayed for HTB-like samples (WMo-1, WMoV-1 and WVMo-2); introduction of vanadium decreases total acidity (more pronounced on mass-bases) but it increases the Brϕnsted-to-Lewis acid sites ratio. Moreover, the augmented molybdenum content in the pseudo-crystalline structures (WMo-2, WMoV-3 and WMoV-4), brings about an increase in total acidity, but it depresses the presence of Brϕnsted-type acid sites. These evidences show that the introduction of redox elements (i.e. vanadium and molybdenum) in the WO_3 framework plays also a role on the nature of acid sites. Overall, it is important to point out that all the mixed-oxides studied have a predominant Brϕnsted acid character, therefore emphasizing the role played by these acid sites in the glycerol dehydration step.[31,32]

2. Glycerol oxidehydration

The catalytic behaviour of every sample was studied in the temperature range 270-410°C and at different residence times. It must be mentioned that for all the catalysts and all the reaction conditions explored, glycerol conversion was always complete, as also reported for W-V-Nb-O catalysts;[15,17] it was demonstrated that even at very low contact time the polyol conversion did not decrease due to the formation of oligomers and ketals (generally grouped as “heavy compounds”). From products trends reported in this work -vide infra-, it is evident that the same phenomenon is also present for all the catalysts here studied. Moreover, as far as the nature of these compounds is concerned, a detailed characterization has already been reported.[17] However, it is worth mentioning that the same kind of compounds were detected among reaction products also for the catalysts here studied, both at low contact time and/or low reaction temperature.

2.1 Catalytic trends at constant feed molar ratio

Table 2 summarizes some of the catalytic results obtained in the oxidehydration of glycerol performed on bi-component W-Mo and tri-component W-Mo-V catalysts. Moreover, Table S1 lists representative reactivity results for each catalyst. Generally speaking, both bi-component catalysts showed always complete glycerol conversion and remarkable acrolein yield; however, only low yields in partial oxidation products (mainly acrylic and acetic acid) were obtained along with high yields in both heavy compounds and CO_x. At contact time 0.4s and 330°C, WMo-2 (which showed a better catalytic performance than WMo-1) allowed obtaining 12% acrylic acid selectivity plus 28% acrolein (Figure 4); the highest heavy compounds selectivity (35%) was reached at 270°C, thus decreasing in favour of carbon oxides at higher temperature. The relevant formation of heavy compounds, particularly for sample WMo-1, can be attributed to the low Brϕnsted-to-Lewis acid sites ratio; indeed, poor Brϕnsted acid properties are known to bring about partial glycerol dehydration into 1-hydroxyacetone and allylic alcohol, finally favouring their successive ketalization.[15] Moreover, acrolein can also generate heavy compounds by both self-oligomerization and ketalization thorough condensation with glycerol, the latter reactions being catalyzed by the same acid sites needed for the first step of glycerol dehydration.[17] Therefore, since molybdenum alone is clearly inefficient in the fast oxidation of acrolein (as underlined by the high ratio between acrolein and acrylic acid, even for high molybdenum loadings in the catalyst -see WMo-2-), the parallel reactions taking place from the above mentioned molecules and leading to heavy compounds are favoured.

A remarkable improvement in the oxidation of acrolein to acrylic acid is observed for the tri-component samples, i.e. W-Mo-V-O, provided the well-known redox features of vanadium in oxidation catalysis. The introduction of vanadium in the oxide structure, even at low concentration, e.g. WMoV-1, led to a remarkable difference in the catalytic performance. Indeed, at low temperature, acrylic acid selectivity increased almost three times (from 7% to 18%) and its maximum shifted from 330°C to 270°C, pointing out the superior redox properties of vanadium in comparison to molybdenum; on the other hand, increasing the temperature, total combustion was favoured. Catalyst WMoV-3 is the material that gave the highest acrylic acid selectivity (31%) at the lowest temperature. The heavy compounds selectivity set between 7% and 12% and the CO_x varied between 40% and 50% selectivity; at temperature higher than 330°C, acrylic acid selectivity decreased, partially in favour of carbon oxides but to some extent also in favour of acrolein and heavy compounds, suggesting that at higher temperature the oxygen introduced in the feed is not enough to oxidize acrolein. All in all, a remarkable note for the catalytic performance of WMoV-3 is that acrylic acid selectivity is almost identical on a wide range of temperature (from 270°C to 330°C); comparing this catalyst with the ones already reported in literature for the same reaction (vide-supra), it is evident that this behaviour represents an important step forward for the design of catalysts more suitable for industrial scale-up. Indeed, in oxidation catalysis the precise control of temperature all along the fixed-bed reactor length represents a very challenging task at industrial scale.

Thus, combination of molybdenum and vanadium leads to a better control of the oxidative properties of the catalysts, smoothing the oxidizing strength of vanadium. In regard to acrylic acid selectivity as a function of temperature, a similar trend to WMoV-3 was registered for WMoV-4, but at a lower contact time (0.15s) (Figure S2,B); indeed, from 270°C to 410°C acrylic acid yield varied of only few percentage points, from 22% to 28%. Moreover, at low temperature the carbon oxides yield was much lower in the latter case, even if there was no gain in acrylic acid yield, since the difference is basically accounted in higher formation of heavy compounds; however, comparing WMoV-3 and WMoV-4 tested at contact time 0.15s (Figure S2), the latter sample leads to higher yields into acrylic acid and lower yields to CO_x. Finally, comparing WMoV-3 and WMoV-4 tested at contact time 0.4s (Figure 4) higher acrylic acid yields were obtained in the former case as long as lower yields into acrolein, and much lower yields into heavy compounds, corresponding to higher CO_x yield. Concluding, higher loadings of vanadium improve the oxidation process but lead to total oxidation products at higher temperature and residence time; on the other hand, high amounts of molybdenum depress both glycerol selective dehydration and acrolein oxidation, favouring the parallel reactions leading to heavy compounds.

2.2 Productivity

Because of the wide range of physical-chemical properties of the complex oxide catalysts here reported, we calculated the productivity both for acrylic acid (AA) and acrolein (A) (Table 2). Productivity can reveal differences regarding the active phases, therefore making it possible to relate the catalytic performance and the catalysts´ nature. Comparing samples WMoV-1 and WMoV-2, both with an HTB structure, it is possible to figure out the role of vanadium in the catalysts; indeed, on a similar base of molybdenum, the sample richer in vanadium (WMoV-2) improves productivity not only for the partial oxidation product, but also for acrolein. This evidence points out once again the role of vanadium in the acrolein oxidation, but it also reflects that a fast oxidation step is mandatory so as to limit the parallel reaction leading to heavy compounds. Molybdenum is also crucial in the oxidation process; indeed, moving from WMoV-1 to WMoV-3 (having similar amount of vanadium but higher content of molybdenum) acrylic acid productivity is greatly improved. Moreover, the higher amount of molybdenum (WMoV-4 vs. WMoV-2) leads both to a variation in the elements distribution and nature of acid sites (from Brϕnsted to Lewis) which depress the overall oxidehydration process, as highlighted by the abrupt overall productivity drop (AA+A) per meter square of catalysts; on the other hand, acrylic acid productivity on molar bases increases from 0.059 to 0.066 h^{-1} due to the increased surface area (from 12 to 22 $m^2\ g^{-1}$).

The role of the crystal structure can also be outlined from productivity trends calculated on mass and surface area basis. For the tri-component catalysts, AA productivity, on mass- and surface area-bases, has its maximum located in different positions, i.e. WMoV-3 and WMoV-2, respectively. This means that the best catalyst, in terms of productivity per specific surface area, is WMoV-2; however, because of its low area, the productivity remains scarce on mass-bases. Therefore, the pseudo-crystalline structure for low vanadium- and high molybdenum-content plays an important role in the catalysts productivity per gram of catalyst. On the other hand, the relative distribution of the elements appears to have the major impact on the catalytic performance: productivity depends on the oxide composition, whether in the HTB or in the pseudo-crystalline phase.

For bi-component (W-Mo) catalysts, acrylic acid productivity is relatively high due to the low surface area; however, it is low per gram of catalyst. Moreover, the high overall acrolein productivity underlines the insufficient redox properties of V-free catalysts (acrolein remains mainly unconverted). Finally, so as to gain a wider picture on the role of tungsten, it is of interest to compare our results with the ones recently published by L. Shen et al.[18] using Mo/V oxides (without tungsten), prepared by slurry synthesis (i.e. $Mo_6V_9O_{40}$- and MoO_3-phases) presenting relatively low surface area (10-12 m^2/g). When glycerol was made react on these oxides, low carbon balances were obtained due to poor acid properties of the catalysts (both as total acidity and most likely as Brϕnsted-to-Lewis acid sites ratio), as long as a wide range of C3 and C2 products.

Therefore, the above mentioned evidences on W-Mo- and W-Mo-V-catalysts make it clear that: (i) a high amount of Brϕnsted acid sites is needed to perform selectively the glycerol dehydration step into acrolein, highlighting the fundamental role of tungsten, (ii) the specific productivity of the catalysts is governed by the elements abundance in the oxide frame, whether it is composed of an HTB- or pseudo-crystalline-structure, (iii) the pseudo-crystalline structure has a role only in determining the catalyst productivity, due to its influence on surface area.

2.3 Influence of the feed composition and time on stream

The catalytic performance of WMoV-3 was studied as a function of inlet feed composition as it gives the highest acrylic acid yield and productivity at the lowest temperature and it is stable along a wide range of temperature. Indeed, we recently reported that high oxygen partial pressure enhances the re-oxidation process of the catalyst, boosting the selectivity in the partial oxidation product (acrylic acid).[17] Moreover, in order to prove the beneficial effect of molybdenum for the oxidation step, we also analysed the catalytic behaviour of the WV-oxide catalyst, in the same reaction conditions (see table 1), that showed the best catalytic performance under oxygen-to-glycerol feed molar ratio 4/2.[14] These catalytic tests were carried out at contact time close to 0.4s and 290°C, to get the best balance between the partial oxidation of acrolein into acrylic acid and its total combustion into carbon oxides, so the acrylic acid yield maximum (Figure S3 and reff. 9-10). In catalytic tests presented in Figure 5 (A and B), glycerol and water molar ratio in feed were kept constant, 6% and 40%, respectively. Meanwhile oxygen and inert gas partial pressures were changed to vary the oxygen molar ratio and keep constant the overall contact time. Generally speaking, excluding the oxygen-to-glycerol molar ratio 6/6, it is evident that WMoV-3 (figure 5A) is much more efficient in the partial oxidation of acrolein into acrylic acid than WV (figure 5B); indeed, acrylic acid increases at a much higher pace, moreover the acrylic acid-to-acrolein ratio is substantially higher.

At oxygen-to-glycerol molar ratio 12/6, WV reached only 35% acrylic acid selectivity, whereas WMoV-3 outperformed up to 51%. It is worth of note saying that the acrylic acid yield for the tri-component catalyst is one of the highest values so far reported in literature for the one-pot synthesis of acrylic acid from glycerol using a single multifunctional catalyst. Interestingly, the only worst catalytic performance of WMoV-3 compared to WV was obtained at oxygen-to-glycerol molar ratio 6/6; indeed, it is evident the higher formation of heavy compounds as long as lower acrylic acid selectivity. This phenomenon can be ascribed to the higher acidity of Mo-containing catalyst (76 vs. 129 $\mu mol_{NH3}/g_{cat}$), the latter properties influencing more the heavy-compounds formation when the oxidation step is slower. Indeed, it can be inferred that if the oxidation step is slow, the higher acidity impedes the fast desorption of the intermediately formed acrolein, therefore favouring the parallel reaction leading to heavy compounds. Overall, it is worth mentioning that oxygen conversion for both catalysts constantly decreases as a function of oxygen concentration (table S3). However, in the case of WMoV-3, oxygen conversion is always higher, suggesting that the presence of molybdenum ease the oxidation process, making it possible to reach higher acrylic acid yields.

Very similar catalytic behaviour was also observed for both catalysts when the oxygen-to-glycerol molar ratio was set constant -equal to 2- (Figure S4, A and B); indeed, heavy compounds yield decreased mainly in favour of acrylic acid than CO_x. Therefore, it is confirmed that high partial pressures of oxygen play the fundamental role of accelerating the catalyst re-oxidation process. Indeed, when acrolein was made react on WMoV-3 in the same reaction conditions (Fig. 6) a different behaviour was registered, since increasing the partial pressure of both oxygen and glycerol -but keeping constant their ratio- the acrylic acid selectivity decreased regularly in favour of carbon oxides. Finally, getting closer to the flammability point (ratio 6:18), it is evident that total oxidation of acrolein to CO_x is increased. All in all, comparing the latter trends with the ones obtained for glycerol and the different COx yields got in the two experiments, it can be inferred that glycerol strongly interacts with the catalyst, leading to saturation of the surface; as a consequence, (i) the availability of the redox sites is limited, which implies the need for high partial pressure of O_2 to guarantee a sufficient concentration of oxidizing sites, (ii) glycerol residence time on the catalyst surface is augmented, leading to its direct oxidation (scheme 1).

Finally, the catalytic behaviour of WMoV-3 was studied as a function of the time on stream -ToS- (figure 7), using the same reaction conditions where the maximum acrylic acid yield was registered. Along 70 hours ToS glycerol conversion was always complete, the sum of acrolein and acrylic acid being constant with an average value around 53% and an initial 51% acrylic acid yield; on the other hand, after 90 minutes ToS (that is the time we normally used to study the catalysts behaviour - see experimental section-), acrylic acid yield slowly started to decrease in favour of the aldehyde. Overall, after ca. 28h ToS both products yield reached a stable average value of 42%

(acrylic acid) and 12% (acrolein); the latter values being stable for at least the following 40 hours. Comparing the XRD spectra of fresh and spent sample -after 69h ToS- (figure S5) it is possible to see that a new diffraction peak appears at ca. 26 2θ degrees, the latter being most likely related to partial decomposition of the pseudo-crystalline structure into monoclinic-WO_3. Moreover, comparing Raman spectra of fresh and spent catalysts (Fig. S6), it is revealed the presence of carbonaceous deposits on the surface. Both phenomena could thus be ascribed as responsible for the changes in product distribution during ToS test. So as to assess the relative importance of the two phenomena, an attempt of regeneration was carried out feeding a mixture of oxygen and nitrogen (molar ratio 5:95) at 350°C for 2 hours, contact time 0.4s. As demonstrated by Raman spectra of regenerated catalyst (figure S6) the carbon deposits were effectively removed by the oxidation treatment; on the other hand, once the regenerated catalyst was used to continue the ToS test, acrylic acid selectivity improvement was minimum (plus 2-3%). Hence, the change of the crystalline phase is clearly the key-factor governing the catalyst deactivation. Comparing the variation observed for the crystal structure of the W-Mo-V catalyst to W-V-Nb oxide previously studied,[12] it is evident the stabilizing role played by niobium; indeed, Nb-containing catalyst preserved the structure after an analogous ToS test. This evidence suggests that niobium might play a similar role in both pseudo-crystalline- and HTB-structures as reported for the M1-phase in Mo-V-Nb-Te catalysts.[20]

Conclusions

Glycerol oxidehydration on a single catalyst is a challenging process from the catalyst design stand-point. In this study a new class of complex W-Mo-V-oxides, strongly related to the hexagonal tungsten bronzes, is reported. The physical-chemical properties and the catalytic performance make it clear the main role of each element in the oxide frame: tungsten dehydrates glycerol to acrolein, vanadium oxidizes acrolein into acrylic acid and molybdenum moderates the strong oxidizing properties of vanadium. The atomic ratio of the elements is pivotal for tuning redox and acid properties, but it also plays a role both in the size of the crystals and their long-range distribution, finally influencing the catalysts' productivity. High oxygen feed molar ratios help the catalyst re-oxidation step and allowed obtaining acrylic acid yield as high as 51% on the WMoV-3 catalyst, whereas the Mo-free sample (i.e. WV) did ot overtake 35% yield into the acid monomer. Acrolein oxidation tests evidence that direct oxidation of glycerol and acrolein also take place. Time on stream test (ca. 70h) on WMoV-3 reveals a stable overall yield for acrolein and acrylic acid. Under reaction conditions, evolution of the crystal phase leads to a slight inversion in the yields of the two consecutive products along the first 5h ToS. However, a stable catalytic behaviour was observed for more than 40 hours ToS.

Experimental Section

Catalysts' synthesis

The W-V-Mo catalysts, were prepared hydrothermally from gels obtained from the aqueous solution of corresponding salts: ammonium metatungstate hydrate (≥85 wt% WO_3 basis, Sigma-Aldrich), vanadium (IV) oxide sulfate hydrate (≥99.99%, Sigma-Aldrich) and ammonium heptamolybdate tetrahydrate (GR for analysis, MERCK). The hydrothermal synthesis was carried out at 175°C for 48 h; then the solid was washed and dried at 100°C overnight. We refer to the dried solid as "catalyst precursor". Lastly, the catalyst precursor was heat-treated in N_2 at 600°C for 2 h. Only for selected analysis, the catalyst precursor was heat-treated in N_2 at 800°C for 2h. In the latter case, specific mention of the not-conventional heat-treatment is reported.

Catalysts' characterization

Surface areas were obtained from N_2 adsorption isotherms using the BET method; a Micromeritics ASAP 2000 instrument was used. Samples were degassed in-situ under vacuum at 250°C.
Powder X-ray diffraction patterns (XRD) were collected using a PANalytical X'Pert PRO diffractometer with CuKα radiation and an X'Celerator detector in Bragg-Brentano geometry.
The quantitative EDS analysis was performed using an Oxford LINK ISIS System attached to a JEOL 6300 electron microscope with the SEMQUANT program, which introduces the ZAF correction. The counting time was 100 s for major and minor elements.
Infrared spectra were recorded at room temperature in the 300-4000 cm^{-1} region with a Nicolet 205xB spectrophotometer equipped with a Data station at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans. Raman spectra were obtained with an "in via" Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 514 nm from a Renishaw HPNIR laser with a power of approximately 15 mW on the sample.
Experiments of Temperature-programmed desorption of ammonia (TPD) were carried out on a TPD/2900 apparatus from Micromeritics. A 0.30 g sample was pre-treated in a He stream at 450°C for 1 h. Ammonia was chemisorbed by pulses at 100°C until equilibrium was reached. Then, the sample was fluxed with a He stream for 15 min, prior to increasing the temperature up to 500°C in a helium stream of 100 mL min^{-1} and using a heating rate of 10°C min^{-1}. The NH_3 desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer following the characteristic mass of ammonia at 15 a.m.u.
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 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).

Reactivity experiments

Reactivity experiments for glycerol and acrolein transformation were carried out using a continuous flow reactor made of glass, operating at atmospheric pressure. For each condition, all the reaction parameters are always listed in each figure. A catalyst amount ranging from 0.10 to 0.30 g was loaded in powder form. Residence time (calculated as the ratio between catalyst volume (mL) and total gas flow (mL/s), the latter being measured at room temperature) was varied. Inlet feed molar ratios between reactants were also changed according to the desired compositions. If not differently specified, the catalytic results were obtained after 90 min reaction time.

For both glycerol oxidehydration and acrolein oxidation, the effluent stream was bubbled through two in-series abatement devices, which were filled with water (but in some cases anhydrous acetone was used, for the identification of compounds which are less soluble in water) and held at a temperature of 0-2°C; a third refrigerated condenser was left without any solvent. After this abatement, the gaseous stream, still containing oxygen and carbon oxides, was fed to an automatic sampling system for gas-chromatography (GC-TCD) analysis. The water solution containing the unconverted glycerol and reaction products was analyzed by GC, using a Hewlett-Packard 5890 instrument equipped with a FID detector. A semi-capillary wide-bore OV 351 (polyethyleneglycol treated with terephthalic acid) column was used for the separation of condensed compounds.[12] Two wide-bore columns were used for the separation of non-condensable products: a Molecular sieve 5A for oxygen and CO, and a Silica Plot for CO_2 (oven temperature 80°C). Compounds were identified by means of both GC-MS and the injection of pure reference standards for the comparison of retention times in the GC column. A few unknown compounds were eluted in the GC column; we attributed to these compounds the same response factor of the corresponding known compound with the closest retention time. In the figures included with this paper, minor identified products and unknown compounds eluted have been grouped together under the heading “Others”. Cyclic ethers were also sometimes produced; however, since with the chromatographic set-up used it was not possible to perfectly resolve each peak correspondent to cyclic ethers, both the latter compounds and heaviest compounds not eluted in the GC column (left as residues on both catalyst surface and reactor walls), were quantified as the lack to the total C balance and labelled as “Heavy compounds”.

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