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

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The design of suitable catalysts for the one-pot conversion of glycerol into acrylic acid (AA) is a complex matter, as only finetuning of the redox and acid properties makes it possible to obtain significant yields of AA. However, fundamental understanding behind the catalytic phenomenon is still unclear. Structure–reactivity correlations are clearly behind these results, and acid sites are involved in the dehydration of glycerol into acrolein with vanadium as the main (or only) redox element. For the first time, we propose an in-depth study to shed light on the molecular-level relations behind the overall catalytic results shown by several types of V-containing catalysts. Different multifunctional catalysts were synthesized, characterized (>X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, temperature-programmed reduction, and temperature-programmed desorption of ammonia), and tested in a flow reactor. Combining the obtained results with those acquired from an in situ FTIR spectroscopy study with acrolein (a reaction intermediate), it was possible to draw conclusions on the role played by the various physicochemical features of the different oxides in terms of the adsorption, surface reactions, and desorption of the reagents and reaction products.

Introduction

Acrylic acid (AA) is the fundamental building block for the production of polyacrylates, that is, the chemical backbone of many kinds of plastics, rubbers, synthetic fibers, an so on.^[1] Nowadays, the world production of AA is estimated to be approximately 5–6 million tons per year, and its demand is foreseen to increase steadily, mainly owing to the growing needs of emerging economies, particularly China.^[2] Most of the current AA productions use propylene as the raw material, in turn synthesized from naphtha steam cracking or, in minor amounts, by the dehydrogenation of propane.^[3] The price of propylene is constantly increasing as a result of a shift in the

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feed of crackers from naphtha to natural gas, mainly ethane, and the increasing demand for polypropylene.^[4]

Provided with these market trends and the environmental concerns linked to the utilization of fossil feedstocks, alternative "green" routes have been explored in the last decade to produce AA from renewable resources.^[2,5-7] Amongst the various options, one of the most explored paths has been the utilization of bioglycerol as a starting material, produced as a coproduct of biodiesel synthesis.^[5,8-10] Particularly, great attention has been focused on substituting the first step of conventional AA production, that is, partial oxidation of propylene to acrole-in, with glycerol acid catalyzed dehydration to the same aldehyde. Indeed, this would be a drop-in technology that could be implemented in the existing two-step processes to produce AA from propylene. Nonetheless, if the AA demand keeps increasing, the construction of new plants would be required to avoid running existing facilities above their optimal capacities.

In the latter scenario, the ideal option would be to synthesize acrylic acid from glycerol (Scheme 1) with as little economic and engineering effort as possible.^[2,5] From this viewpoint, the ideal solution would be to perform the transformation of



Scheme 1. The two reaction steps required for the transformation of glycerol into acrylic acid.



glycerol into acrylic acid as a single-step (i.e., one-pot) reaction by using a multifunctional catalyst. However, the design of multifunctional acid and redox catalysts for the dehydration of glycerol and the partial oxidation of acrolein is a major challenge. The first attempts to perform the one-pot reaction were reported both in patents and in the open literature;^[11-13] however, the AA yields on single catalysts were always low (< 15%). After these first studies, catalysts related to the family of perovskites greatly improved the AA yields, up to 28%;^[14,15] nevertheless, both the productivities and the overall catalytic

performance remained unsatisfactory. In the last few years, many efforts have been made to improve the performance of catalysts for the one-pot oxidehydration of glycerol to AA. Overall, catalysts related to metal-oxide bronzes seem to be the best-performing materials, and they are capable of efficiently transforming glycerol into acrylic acid with yields > 50% and productivities of industrial relevance.^[16–19] None-theless, other systems have shown promising results, such as V-doped zeolites^[20,21] and V-P oxides.^[22,23]

Interestingly, the common point of all these catalytic systems is the presence of vanadium as one of the main (or only) redox elements; however, despite this leitmotif, the catalytic behavior of these mixed oxides is fairly different. As we recently reviewed,^[24] the impressive versatility of vanadium as a catalyst for different gas-phase reactions is a remarkable feature of this element, probably unique in the entire periodic table. The environment that characterizes the vanadium contour in the different catalytic systems makes it possible to forge its properties, weak-

ening some of them in favor of others. Taking into account the lack of molecular-level information on the one-pot oxidehydration reaction of glycerol, that only recently started to be fulfilled,^[25] we present herein an in-depth study that aimed to link the results obtained by reactivity tests performed in a flow reactor with those obtained by in situ FTIR spectroscopy studies by using the reaction intermediate (i.e., acrolein), as well as Xray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, temperature-programmed reduction and temperature-programmed desorption of ammonia mass spectrometry (NH₃-TPD-MS). Representative multifunctional V-containing catalysts were considered: one, hexagonal tungsten bronzes (HTBs) with in-framework or extra-framework vanadium species; two, zeotype materials, that is, modified-AIPO₄-5 catalysts^[26] with in-framework and extra-framework vanadium species; three, a commercial vanadyl pyrophosphate (VPP) catalyst.^[27] Remarkable structure-reactivity correlations were revealed for the one-pot oxidehydration of glycerol that shed light on the different behaviors of vanadium as a function of the physical and chemical features of the oxide in which it was present. V-free parent materials were also studied as reference materials for both characterization and catalytic tests purposes.

Results and Discussion

Physicochemical properties of the oxides

All the samples studied were analyzed by X-ray diffraction (XRD) (Figure 1). The tungsten-based oxides (Figure 1, patterns a-c) present the typical pattern of the hexagonal phase (JCPDS: 33-1387). The V-exchanged HTB, that is, VO-WO_x (Figure 1, trace b), presents a structure basically identical to that of the parent material, WO_x (Figure 1, trace a). However,



Figure 1. XRD patterns of the catalysts: a) WO_{xr} b) $VO-WO_{xr}$ c) WV, d) CoAPO, e) VCoAPO, f) $VO_x/VCoAPO$, and g) VPP. (\bullet) indicates V_2O_5 diffraction peaks.

the diffraction peaks of these two samples are slightly broader than those of hexagonal tungsten/vanadium oxide, WV (Figure 1, trace c). This might be due to small differences in morphology (different growth along the crystalline planes) and/or incomplete crystallization of the hexagonal phase. A role might also be played by the lower heat-treatment temperature used for WO_x and VO-WO_x relative to that used for WV (i.e., 450 vs. 600 °C); indeed, if heated at temperatures >450 °C, the former two structures evolve into monoclinic forms (i.e., WO₃ and V-doped WO₃). As previously demonstrated by high-resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED), as well as morphological and spectroscopic analyses,^[18, 28, 29] there is remarkable evidence that proves that the majority of vanadium in VO-WO_x is incorporated as extra-framework species. Only if another transition element (e.g., V, Nb, Mo, Ti) enters the hexagonal tungsten oxide framework is the HTB structure stable at temperatures significantly higher than those bearable by the material built up by only W atoms (WO_x). Hence, it can be concluded that vanadium is mainly present in VO-WO_x as extra-framework species, either deposited on the external surface or inside the hexagonal channels. Taking into account the washing of the catalyst after the ion-exchange process (see the Experimental Section), and the Raman spectra (see below), the latter option is more likely. The modified AIPO₄-5 systems (Figure 1, patterns d-f) present the characteristic pattern of



zeotype materials with AFI structure (JCPDS: 41-0044), which confirms the correct preparation of the AIPO₄-5 catalysts. For both CoAPO and VCoAPO catalysts, no changes are observed in the diffraction patterns, which confirms the insertion of cobalt and vanadium in the oxide framework as tetrahedral units.^[30] However, if an additional amount of vanadium is added to the VCoAPO catalyst by wet impregnation (sample VO_x/VCoAPO; Figure 1, pattern f), extra-framework vanadium species are formed as V₂O₅, which are responsible for the additional diffraction peaks observed for the latter sample. The

XRD pattern of the VPP catalyst (Figure 1, pattern g) shows the presence of the characteristic phase (VO)₂P₂O₇; the lack of additional peaks confirms that no other V-P-O phases constitute the bulk phase of the catalyst.^[27]

Raman spectroscopy was used to improve the understanding on the structure of the various catalytic systems prepared, particularly to shed light on the nature of the vanadium species in the HTB-like materials.^[31-33] If vanadium enters the HTB framework, a new band at $\tilde{\nu} = 970 \text{ cm}^{-1}$ appears in the Raman spectrum (sample WV, Figure 2a). This can be related to the greater number of W-O bonds generated by



cludes the presence of V=O stretching assigned to 2D vanadi-

um species; moreover, the absence of a sharp signal at $\tilde{v} =$

995 cm⁻¹, as well as more broad features at $\tilde{\nu} =$ 700, 530, 500, 400, and 300 cm⁻¹, exclude the presence of V₂O₅ nanoparti-

cles.^[32-34] Considering these results, it is possible to conclude

that the majority of vanadium is present in VO-WO_x as extra-

framework species, precisely as V ions located inside or, most

XPS measurements were performed to shed light on the oxi-

dation state of V on the surface of catalysts (see Figure 2b and

likely, in the mouth of the hexagonal channels.



Figure 2. a) Raman and b) V2p_{3/2} XPS spectra of selected catalysts. CPS = counts per second.

a structural defect as a result of vanadium incorporation and/ or V–O bonds associated to polymeric V–O–W chains. $^{\scriptscriptstyle [14,28]}$ In the VO-WO_x sample, this band is very weak but is not completely absent; moreover, the main bands located at $\tilde{v} = 694$ and 819 cm⁻¹ are shifted to lower frequencies relative to the main bands of the pristine WO_x sample, as in the case of substituted-HTBs.^[28]

Hence, although the majority of vanadium occupies extraframework positions, as previously discussed, it can be inferred that a minor portion of it might replace the in-framework W atoms, most likely during heat treatment through a solid-solid reaction. Overall, the absence of a band at $\tilde{\nu} = 1035 \text{ cm}^{-1} \text{ ex-}$ Table 1). Different states of V ions can be evidenced; both V^{5+} (binding energy (BE): 517.1 eV) and V^{4+} (BE: 516.1 eV) ions can be detected on the WV sample, whereas a higher V^{5+}/V^{4+} surface ratio is shown for the extra-framework V species in the ion-exchanged sample, VO-WO_x. Considering that the ion exchange was performed by using vanadyl ions (VO²⁺), the XPS results point out a partial oxidation process during catalyst preparation, consistently more severe in the case of the extra-framework V species. Moreover, the VPP catalyst presents V⁴⁺ as the predominant species, but the presence of V^{5+} is also significant, despite the fact that the XRD pattern only shows the presence of (VO)₂P₂O₇; this observation agrees with previous reports by other authors,[35-37] who attribute the presence of V^{5+} species to the coexistence of VOPO₄ domains in addition to (VO)₂P₂O₇ on the surface of the catalyst. Finally, the VCoAPO sample shows both V^{5+}/V^{4+} ions, whereas V^{5+} is mainly observed on the VO_x/VCoAPO sample. The high BE of

 V^{5+} in both zeolite-type samples (518.8 eV) is due to high dispersion of the V ions in the lattice framework.[38]

The redox and acid properties of the prepared materials were assessed by temperature-programmed reduction (H₂-TPR) and NH₃-TPD-MS experiments, respectively (Figure 3). As previously reported,^[14] HTB-like materials present two main reduction peaks: one between 450 and 500 °C and another at temperatures $> 550 \,^{\circ}$ C.

Relative to WV, the ion-exchanged sample (VO-WO_x) is reduced at higher temperatures, in accordance with the presence of extra-framework V ions. In-framework V species in the VCoAPO sample are reduced at temperatures < 500 °C,^[38]



Figure 3. H_2 -TPR (a) and NH₃-TPD-MS (m/z = 15) patterns (b) of the catalysts: A) WV, B) VO-WO_x, C) VCoAPO, D) VO_x/VCoAPO, and E) VPP.

whereas the extra-framework V_2O_5 particles in the $VO_x/VCoAPO$ sample are reduced only at higher temperatures. Finally, VPP presents a small and broad reduction peak between 350 and 500 °C and a major reduction peak at a high temperature.^[22] The NH₃-TPD-MS experiments highlight that ion exchange with V ions has a minor impact on acidity if the acidity of VO-WO_x is compared to that of its parent material WO_x. Indeed, the NH₃-TPD profiles (and therefore their total acidity, see Table 1) are quite similar. VCoAPO and VO_x/VCoAPO also have similar profiles; however, the extra-framework V species considerably affect the overall acidity ($\approx\!-25\,\%$). Despite the fact that the acidity on the mass bases of the zeotype materials is higher than that on the modified-HTBs, the acid density (acid sites per m² of surface area) is actually consistently lower for the former materials. The TPD results also suggest that the VPP catalyst has acidic character (in terms of the strength of the acid sites) similar to that of WV, but approximately half its density of acid sites.

Catalytic tests

The studied materials were used as catalysts for the transformation of glycerol in the gas phase. As an explorative test, the contact time optimal for WV (\approx 0.4 s, see Ref. [17]) was also used for the other oxides. Preliminary studies were performed by using the CoAPO catalyst, without vanadium (Figure S1, Supporting Information); despite the acid properties of this material, glycerol conversion was complete only at temperatures \geq 360 °C and no acrylic acid was formed. Moreover, significant amounts of heavy compounds were produced (selectivity between 40 and 50%). However, the addition of V species consistently improved the activity of the catalyst, as in all cases and for all temperatures, glycerol conversion was always complete for both VCoAPO and VO_x/VCoAPO (Figure 4). This is in line with an increase in both the acid (Table 1) and redox sites favoring an increase in activity owing to the formation of

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oxidation products. Furthermore, VPP and WV both always showed complete conversion of glycerol. The glycerol dehydration step to acrolein has been the focal point of a vast number of reports in the literature,^[18,39–43] and there is a general consensus on the pivotal role played by Brønsted acid sites to dehydrate glycerol selectively to acrolein. The significant presence of these sites is known for all the catalytic systems reported herein, that is, HTB-like materials,^[18] CoAIPO₄-5,^[44] and VPP,^[45] and this explains the high conversions and selectivities to acrolein (and, in turn, acrylic acid) obtained for WV, VCoAPO, and VPP.

WV, as for most of the previously reported substituted-HTBs, displayed the highest acrylic acid yield at low temperature, but the yield decreased steeply upon increasing the temperature, in favor of carbon oxides. Differently, VCoAPO showed an acrylic acid maximum at 330 °C; at higher temperatures, heavy compounds selectivity decreased not only in favor of CO_x , but also to acrolein to a minor extent, possibly

as a result of the scarce presence of oxygen at higher temperatures (O₂ conversion \approx 94% at 390 °C). Taking into consideration the product distribution observed for VO_x/VCoAPO and comparing it to those observed for VCoAPO, the extraframework vanadium species seem to: one, block the more active in-framework V sites; two, enhance total oxidation to carbon oxides; three, be completely inactive towards the selective oxidation of acrolein to acrylic acid. It is of interest to compare our results to those obtained by others using V-impregnated zeolites.^[20,21] Indeed, although extra-framework vanadium species were also present in the latter materials, acrylic acid selectivities up to 25% (5%V-impregnated zeolite beta)^[21] and 17% (V2O5/MFI)[20], respectively, were obtained. Despite the fact that V₂O₅ particles were clearly present in those catalysts, the higher production of AA can be attributed to better dispersion of V, as pointed out by XPS analyses.^[21]

The industrial VPP catalyst displayed very peculiar catalytic behavior, as some aspects were similar to those of the VCoAPO catalyst but others were completely opposite to those of the WV catalyst. The CO_x selectivity, at all the temperatures investigated, was the lowest among all the catalysts; however, what is mainly remarkable is the increase in the selectivity to acrylic acid at high temperatures (maximum 16% at 390 °C), that is, at which all the HTB-like catalysts showed minimum values. As a consequence, the acrolein yield decreased, as it was partially and totally oxidized to acrylic acid and CO_x .

To deepen the knowledge of the catalytic behavior of the most active catalysts, that is, WV, VCoAPO, and VPP, catalytic tests as a function of feed molar ratios were performed, as previously reported for other kinds of substituted-HTBs.^[17, 18] However, to better evaluate the catalytic performance of each oxide, preliminary studies on the influence of contact time were undertaken (Figure S2), which proved that VCoAPO had its optimal contact time at approximately 0.4 s (as WV), whereas that of VPP was located at higher values, approximately 1 s.

Figure 5 reports the product distribution for each mixed oxide as a function of feed composition (the glycerol-to-



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Figure 4. Variation in the selectivity to the main reaction (acrylic acid, acrolein, carbon oxides, and heavy compounds) products with reaction temperature over the WV, VCoAPO, VO_x/VCoAPO, and VPP catalysts. Glycerol conversion was always complete. Feed composition (mol%): glycerol/oxygen/water/nitrogen = 2:4:40:54. Contact time 0.4 s. Acetaldehyde, acetic acid, and other compounds formed with the following selectivities on each catalyst: VCoAPO 15– 25%, VPP and VO_x/VCoAPO 11–18%, WV 8–12%. Among the "other compounds", hydroxyacetone was also present. However, numerous unknown species also formed (see the Experimental Section).



Figure 5. Oxidehydration of glycerol as a function of feed oxygen/glycerol molar ratio on a) WV, b) VCoAPO, and c) VPP. Glycerol conversion was always complete. Symbols: acrylic acid (\blacksquare), acrolein (\bigcirc), CO_x (\triangle), heavy compounds (\blacktriangledown). Other compounds detected but not reported in the plot: 1) WV: acetic acid and acetaldehyde 2–3 %, unknown compounds 2–3 %; 2) VCoAPO: acetaldehyde + acetic acid 8–17 %, unknown compounds 3–7 %; 3) VPP: acetic acid ≈10 %, unknown compounds 2 %. Reaction conditions: a) *T*=290 °C, τ (contact time)=0.4 s; b) *T*=330 °C, τ =0.4 s; c) *T*=390 °C, τ =1 s. Water concentration in feed was 40 mol%.

oxygen molar ratio and water concentration in the feed were kept constant) by using the optimal temperature and contact time for each catalyst (see details in the figure caption). WV showed its maximum acrylic acid selectivity (35%) under glycerol-rich conditions (feed composition glycerol/oxygen/water/ nitrogen = $6:12:40:42 \mod \%$), as previously observed for all the

other HTB-like catalysts.^[17,18] VCoAPO did not improve its performance by varying the feed composition, as the acrylic acid maximum (12%) was found to lie under the previously explored conditions, that is, glycerol/oxygen molar ratio of 0.5 (2:4 mol%). Also in this case, VPP showed behavior that was opposite to that of the HTB-like catalysts, and it presented the maximum acrylic acid yield (28%) at low glycerol concentrations (feed composition glycerol/oxygen/water/nitrogen = 1:2:40:57 mol%).

At higher pressures of the reactants, both partial and total oxidation were hampered, which provoked an increase in the intermediate product (acrolein) and finally the formation of heavy compounds.

At this stage, it is worth mentioning that V-P oxides were previously studied by others for this reaction.^[23] Among the V-P-O materials prepared, it was found that the one treated at 800 °C was the best performing phase, with acrolein selectivity up to 64% but only trace amounts of acrylic acid. Moreover, regardless of the catalyst thermal treatment, acrylic acid was always produced in trace amounts. Although the different results obtained in this work upon using the industrial VPP catalyst could be explained by taking into account the fact that the physicochemical properties (e.g., surface area, heat treatments, preparation method, etc.)^[22] of the latter catalyst are different than those of the previously reported V-P oxides, it is safe to say that the major role is actually played by the reaction conditions. Indeed, upon testing the industrial catalyst under the same reaction conditions as those reported in Ref. [23], the catalytic performance was almost identical for both catalysts (see Figure S3).

To further explore the structure-reactivity correlations of multifunctional catalysts for the oxidehydration of glycerol, the catalytic behavior of the WV sample was compared to that of the ion-exchanged catalyst, VO-WO_x (Figure S4b). Despite the formation of acrolein on VO-WO_x, acrylic acid was formed in just minor amounts (3%), whereas CO_x was formed in remarkable amounts. This may be related to the lower redox behavior of the V ions, which decreases the oxidation rate of the acrolein intermediate and favors secondary reactions (finally leading to heavy compounds). Despite the fact that the content of vanadium in the ion-exchanged sample was lower than that in WV (VO-WO_x 0.15 vs. 0.21, see Table S1), the distinct catalytic behavior cannot be attributed merely to the different compositions; indeed, previously reported V-containing HTBs with inframework V species and a similar V/W ratio to that in VO-WO_x showed acrylic acid selectivity > 20% under identical reaction conditions (see Ref. [14] and Figure S4A). Moreover, differently from WV, VO-WO_x did not show any significant change in catalytic performance upon exposure to higher partial pressures of the reactants (see Figure S4B). These results seem to point out that the presence of V species in the framework positions enhances the oxidation properties of the transition element. However, as discussed in the in situ FTIR spectroscopy studies (see below), the picture at the molecular level is actually opposite, in which the strong acid sites in VO-WO_x play a major role in the formation of consecutive products owing to strong adsorption of the reaction intermediates. Overall, although the absolute values of the product selectivities might also depend on the real accessibility of the V sites on the different samples (e.g., acrolein and other C3 molecules can enter the micropores of zeolites,^[42] whereas HTBs have only external surface area available for catalysis),^[29] the remarkable differences displayed by the catalysts reported herein as a function of temperature and feed molar ratios open important questions. Despite the fact that all of the studied materials efficiently dehydrated glycerol into acrolein and that they all had V as the only active element to perform the partial oxidation, their catalytic behavior is sometimes opposite. This highlights that close proximity of acid and redox sites (i.e., V ions) at the atomic level is mandatory to efficiently perform the oxidehydration reaction of glycerol on a single catalyst.

In the pursuit of the intimate relations that link the catalyst structure and the catalytic results, in situ FTIR spectroscopy analyses were performed by studying the oxidation of the intermediate product, that is, acrolein, on the different multifunctional catalysts. Attempts were also made to adsorb glycerol on the surfaces of the catalysts, but its high boiling point prevented it from being transferred into the IR cell in a controllable fashion, as previously reported.^[46] This made it impossible to control the stoichiometry of the two reactants, glycerol and oxygen, inside the IR cell. In 2014, C. Sievers and co-workers reported an ex situ method that could be used to overcome this issue with some catalysts.^[43] Indeed, the catalyst could be slurred for 24 h in an aqueous solution of glycerol, and water was finally removed. However, V-based systems are known to leach vanadium species if dispersed in aqueous solutions, which unfortunately made the application of this ex situ method unreliable, if not impossible, in the case of the bifunctional catalytic systems reported herein.

In situ FTIR spectroscopy study with acrolein

In the first step of the one-pot oxidehydration of glycerol, that is, dehydration of glycerol to acrolein, acid sites of specific acid strength and type are required to favor the desired dehydration reaction to acrolein.^[42] The presence of Lewis acid sites and, particularly, Brønsted acid sites is fundamental to direct the dehydration of the secondary hydroxy group selectively to form acrolein.^[43] In the second step, that is, the oxidation of acrolein to acrylic acid, both Lewis acid and redox sites are involved.^[47] Depending on the surface properties of the catalyst (acid–base character, nature of oxygen species, and V surface sites), the adsorbed intermediate species evolve into different products such as acrylic acid, acetaldehyde, acetic acid, and CO_x.^[48]

Preliminary evaluation of the interaction of acrolein with the surfaces of the catalysts was performed under anaerobic conditions at room temperature (Figure 6). For the WV, VO-WO_x, VCoAPO, and VPP catalysts, rather complex IR spectra can be observed after acrolein adsorption. The band at approximately $\tilde{\nu} = 1695 \text{ cm}^{-1}$ can be assigned to the stretching vibration of the C=O moiety interacting with the OH groups (i.e., Brønsted acid sites) on the catalyst surface,^[48] whereas bands at approximately $\tilde{\nu} = 1680$, 1666, and 1650 cm⁻¹ are associated to the same carbonyl group interacting with the Lewis acid sites, mainly V⁵⁺/V⁴⁺ ions, in different oxidation states and/or coordination environments (e.g., tetrahedral, octahedral, polyoxo species, dimers, etc.). Owing to the different crystal structures of VCoAPO and VPP, a different nature of the vanadium ions is expected; in fact, this is observed in the IR spectra (Figure 6).



Figure 6. IR spectra of acrolein adsorbed at 25 °C on selected samples.

The band at $\tilde{\nu} = 1684 \text{ cm}^{-1}$ is the most prominent signal in the spectrum of the VPP sample, whereas in the spectrum of the VCoAPO sample, two bands at $\tilde{\nu} = 1680$ and 1665 cm⁻¹ are observed. From the structural characterization data, VCoAPO and VPP samples are characterized by the presence of V ions in a tetrahedral and a square based bipyramidal coordination environment, respectively, and both of them show a mixed oxidation state of V (V^{5+}/V^{4+}). According to the lower coordination number of the V ions, their acid strength is expected to be lower, which would lead to a lower C=O stretching frequency shift after adsorption of acrolein, as clearly evidenced from the IR spectra. The band at $\tilde{\nu} = 1730 \text{ cm}^{-1}$ observed in the spectrum of the VO_x - WO_x sample is due to a ketone intermediate species formed on the catalyst surface by a secondary surface reaction^[49,50] (Figure 6). Given that the reactivity of the surface oxygen species and their interaction with adsorbed acrolein are key in the reaction mechanism, another in situ FTIR spectroscopy study was performed placing both acrolein and O₂ in contact on the different catalysts surface at room temperature. The evolution of the surface species and molecules desorbed in the gas phase was studied as a function of the catalyst temperature, which was progressively increased (see the Experimental Section).

On the WV catalyst, the adsorption of acrolein at room temperature leads to hydrogen-bonded acrolein ($\tilde{\nu} = 1695 \text{ cm}^{-1}$) and coordinatively bonded acrolein on Lewis surface sites ($\tilde{\nu} =$ 1666 and 1650 cm^{-1}) (Figure 7 a). Given that the hydrogenbonded complex is easily removed from the surface by evacuation, it can be assumed that it does not play an important role in the catalysis of acrolein oxidation. Upon increasing the temperature to 80 °C, a new band appears at $\tilde{\nu} = 1723 \text{ cm}^{-1}$ at the expense of the bands at $\tilde{\nu} = 1666$ and 1650 cm⁻¹. The band at $\tilde{v} = 1723 \text{ cm}^{-1}$ is ascribed to carbonyl-bonded acrolein, referred to as surface complex III by Andrushkevich and Popova.^[48] In complex III, the C=O moiety of acrolein is bound with an O atom that belongs to the oxide framework of the catalyst; this is believed to be the key intermediate for the selective oxidation of acrolein to acrylic acid on mixed-oxide catalysts. At room temperature and before evacuation (see above), the band at approximately $\tilde{\nu} = 1695 \text{ cm}^{-1}$ is assigned to hydrogenbonded acrolein; however, as this species quickly desorbs

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Figure 7. Mechanistic studies performed by co-adsorption of acrolein and oxygen at increasing temperatures on a) WV and b) VO-WO_x. Thin lines correspond to the sample at the given temperature, whereas bold lines correspond to the sample at a given temperature but after cooling the pellet down to 25 °C. TBM = spectrum achieved at 300 °C but by using a turbo molecular pump.

under vacuum, at this temperature (80°C) it must be assigned to another species bearing the C=O moiety and formed from the interaction of acrolein, oxygen, and the catalyst surface. Considering the relatively low temperature (80 $^\circ\text{C})$ and bearing in mind the products observed in the reactivity tests, it is possible to assign this new band to acetaldehyde, formed by oxidative cleavage of the C=C bond of acrolein. At 80 °C, a less intense IR band at $\tilde{\nu} = 1740 \text{ cm}^{-1}$ can also be observed, and it is assigned to a C=O bond corresponding to a ketone functional group^[51] produced as a byproduct of consecutive reactions occurring on the catalyst surface. Upon increasing the temperature to 160 °C, the previous band at $\tilde{\nu} = 1723 \text{ cm}^{-1}$ is no longer detected on the catalyst surface, but it is detected in the gas phase. This band, together with a very weak band at $\tilde{\nu} =$ 1421 cm⁻¹, also present in the re-adsorption spectra, is associated to acrylic acid. On the other hand, the IR bands ascribed to acetaldehyde ($\tilde{\nu} = 1695 \text{ cm}^{-1}$) together with a new weak band at $\tilde{\nu} = 1370 \text{ cm}^{-1}$, grow in intensity; acetaldehyde is also



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partially desorbed into the gas phase. Moreover, a complex set of IR bands at $\tilde{\nu} = 1780$, 1740, 1602, 1540, and 1440 cm⁻¹ is detected on the catalyst surface. Given that these bands remain stable in the cool-down IR spectra, they should be ascribed to surface-adsorbed species. The band at $\tilde{\nu} = 1740 \text{ cm}^{-1}$ (already detected at 80 °C and associated to C=O vibration of adsorbed ketones) has also been reported as the intermediate species toward the formation of adsorbed cyclic anhydride. Indeed, the IR band at $\tilde{\nu} = 1780 \text{ cm}^{-1}$ is characteristic of cyclic anhydride species.^[51] The other bands at $\tilde{\nu} = 1540$ and 1440 cm⁻¹ are due to acetate species, whereas the band at $\tilde{\nu} = 1602 \text{ cm}^{-1}$ is characteristic of a C-O-C bond of a lactone-type compound. All these species are formed because of overoxidation of the initially adsorbed intermediate complexes. Upon increasing the temperature to 240 °C, the formation of acrylic acid and acetaldehyde is favored, both as adsorbed surface species and desorbed in the gas phase. At 300 °C, acrylic acid formation ($\tilde{\nu} =$ 1723, 1635, 1435 cm⁻¹) is strongly enhanced; an additional sharp band detected at $\tilde{\nu} = 1704 \text{ cm}^{-1}$ is symptomatic of acetic acid formation (bending vibration of the carboxylic OH group appears at $\tilde{\nu} \approx$ 1440 cm⁻¹). Acetic acid may be formed by oxidation of acetaldehyde.[52]

To ascertain the influence of molecular oxygen and water vapor in the reaction mixture, the experiment just described was repeated by using the same catalyst, that is, WV, but under anaerobic conditions or in the presence of water (Figure S5). From the results it is clear that lattice oxygen species are the active species for the selective oxidation of acrolein to $AA^{[53]}$ and water helps its desorption^[54] (i.e., it avoids consecutive reactions). However, owing to poorly resolved IR spectra (broadness) in the presence of water, our discussion will focus on the IR spectra of acrolein and O_2 co-adsorption in the absence of water.

Acrolein and oxygen were made to react on the VO-WO_x sample (Figure 7b). Relative to WV and contrary to that observed in the catalytic tests (Figure S4a), the exchanged V ions (extra-framework) seem to increase the reactivity of the surface oxygen species, as the carbonyl-bonded acrolein surface complex and ketone intermediate species ($\tilde{\nu} = 1723$ and 1740 cm⁻¹, respectively) are readily formed if the sample is kept at room temperature for some time (\approx 20 min). Upon increasing the temperature to 80°C, both bands increase in intensity. A further increase in the temperature to 160 $^\circ\text{C}$ favors the gasphase desorption of acrylic acid ($\tilde{\nu} = 1723$, 1611, and 1421 cm⁻¹) and acetaldehyde ($\tilde{\nu} = 1695 \text{ cm}^{-1}$); surface species are also formed ($\tilde{\nu} = 1780$, 1740, 1602, and 1440 cm⁻¹). However, opposite to WV, a further increase in the temperature to 240 °C-300 °C slows down the gas-phase formation of acrylic acid and acetaldehyde, whereas the IR bands associated to strongly adsorbed surface species increases. Acetic acid (gasphase formation 1704 cm⁻¹) is also detected at 300 °C. VO-WO_x presents an important proportion of strong acid sites (see Figure 3) and the highest acid density (as $\mu mol_{NH_3} m^{-2}$) among all the V-containing catalysts reported herein; therefore, the acid sites seem to bind the product intermediates strongly, which hampers their desorption. This hypothesis is supported by the IR spectroscopy study, which highlights hindered desorption of the intermediate carbonyl complexes; this lowers the formation of acrylic acid and increases the formation of heavy compounds and CO_x . Interestingly, the absence of the IR band at $\tilde{\nu} = 1540 \text{ cm}^{-1}$ (associated to a COO^- moiety of an acetate species) can be related to the desorption of those adsorbed species as CO_x as observed in the catalytic tests.

On VCoAPO and VPP, the in situ IR spectra of coadsorbed acrolein and O_2 (Figure 8 a, b) show behavior that is completely different to that of the HTB-like materials; this is not surprising



Figure 8. Mechanistic studies performed by co-adsorption of acrolein and oxygen at increasing temperatures on a) VCoAPO and b) VPP. Thin lines correspond to the sample at the given temperature, whereas bold lines correspond to the sample at a given temperature but after cooling the pellet down to 25 °C. TBM = spectrum achieved at 300 °C but by using a turbo molecular pump.

taking into account the different nature of the surface V species.^[24,30] As a general note, despite the fact that the just-mentioned differences in surface V species leads to slight shifts in the IR bands associated to some adsorbed molecular species, for easier comparison to the previous spectra and to avoid redundancy in the explanation of IR bands, the same IR bands will be used in the following portion of the text (and in the respective figures) to comment on the in situ IR studies. The dis-



crepancies can be easily understood looking at the related figures.

On VCoAPO (Figure 8a), the V ions in the tetrahedral environment clearly show a lower oxygen insertion capability for the partial oxidation of acrolein, which agrees with the absence of acrylic acid in the gas-phase IR spectrum and the absence of the IR band at $\tilde{\nu} = 1723 \text{ cm}^{-1}$ associated to the carbonyl surface complex. A similar observation was reported for another reaction, namely, the oxidative dehydrogenaalkanes.^[55] Instead, tion of acetaldehyde $(\tilde{\nu} \approx 1695 \text{ cm}^{-1})$ partially desorbs into the gas phase. Other species characterized by IR bands are shown at approximately $\tilde{\nu} = 1670 - 1620 \text{ cm}^{-1}$, which correspond to ketone- or C=C-containing species. These results agree with the catalytic data, which indicate that a higher temperature is needed for the formation of acrylic acid because of the lower reactivity of the tetrahedral V ions. Moreover, opposite to V-containing tungsten bronzes (in which V is in octahedral coordination), higher partial pressures of the reactants in the feed do not improve the formation of acrylic acid in the catalytic tests.

VPP behaves similarly to VCoAPO, that is, it shows low oxygen insertion ability without the formation of the carbonylbonded acrolein complex (Figure 8b). Acetaldehyde (IR band at $\tilde{\nu} = \approx 1695 \text{ cm}^{-1}$) is mainly desorbed in the gas phase, which starts at 80 °C. At 240 °C, cyclic anhydride like species form on the catalyst surface ($\tilde{\nu} = 1780 \text{ cm}^{-1}$), and only at 330 °C are small amounts of acrylic acid formed ($\tilde{\nu} = 1723 \text{ cm}^{-1}$), but acetaldehyde (1695 cm⁻¹) remains the main species present in the gas phase. Interestingly, at 390 $^\circ \rm C$ the cyclic compounds ($\tilde{\nu}\!=\!$ 1780 cm⁻¹) decrease, whereas a new broad band appears at $\tilde{v} = 1554 \text{ cm}^{-1}$, which is associated to asymmetric COO⁻ stretching. The coordination of vanadium in VPP catalysts, that is, bipyramidal V^{4+} sites, $^{\mbox{\tiny [24]}}$ can result in oxygen insertion ability that lies in between that of VCoAPO (with V sites presenting tetrahedral coordination) and that of WV bronzes (with V sites presenting octahedral coordination), but high temperatures are required to perform the oxidation of acrolein. Besides, the reason why VPP needs lower concentrations of glycerol to obtain good selectivity to AA (see catalytic tests) can also be attributed to the relatively limited availability of the redox active sites on the surface, a peculiar feature of this catalyst also reported for other reactions.^[56] To have a good fraction of V^{5+} sites available for oxidation (see XPS results, Table 1), it is necessary to keep the partial pressure of the reactants low and the partial pressure of O₂ (relatively) high.

Structure-reactivity correlations

A molecule of glycerol approaching the catalyst surface from the gas phase predominantly reacts with Brønsted acid sites to perform double dehydration into acrolein (Scheme 2, step 1). Acrolein that is produced must quickly desorb or selectively be oxidized; otherwise, the surface acid sites catalyze the formation of several byproducts, such as ketones, cyclic anhydrides,

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Scheme 2. Reaction mechanism for the oxidehydration reaction of glycerol on acid catalysts with vanadium as the active redox element.

and lactone-type compounds. Acrolein that is desorbed in the gas phase can re-adsorb on the catalyst surface to react further (Scheme 2, step 2). However, it is likely that acrolein that remains adsorbed (without intermediate desorption) is preferentially oxidized over the former, which requires the close proximity of both acid and redox sites.

This is particularly true in the presence of glycerol, which is known to adsorb strongly on the catalyst surface and compete with acrolein adsorption.^[18] Once acrolein is formed, Lewis acid sites are mainly responsible to coordinate the interaction of the aldehyde with the nucleophilic oxygen species (i.e., O²⁻) present on the catalyst surface and generated by the presence of V ions.^[57] In this way, an intermediate surface complex, that is, a carbonyl-bonded acrolein, is formed (Scheme 2, step 3). This is the key intermediate for the selective oxidation of acrolein into acrylic acid. In this reaction step, the coordination environment of V and its oxidation state play vital roles; specifically, a higher coordination number of the V ions favors the oxidation of acrolein into AA.^[43] In addition, the presence of V^{5+} can speed up the oxidation step, which can be of special importance to avoid consecutive reactions if working with very reactive species such as acrolein. The presence of in-framework or extra-framework species does not seem to be determinant, provided that the proximity of acid and redox sites is guaranteed.

Although acid sites are not normally involved in the oxidation of acrolein into acrylic acid, they actually control the desorption step of the latter (Scheme 2, step 4). Owing to the strong nucleophilicity of the COO⁻ moiety, if the acidity of the catalyst surface is too strong and the acid density (as acid sites per m² of surface area) too high, the desorption step is impeded. In the last case, consecutive reactions on acid and/or redox sites lead to oligomerization and total oxidation. This observation is remarkable, as it points out that the one-pot oxidehydration of glycerol can be efficiently performed only by using



catalysts that possess acid sites of sufficient strength and density to perform the dehydration step, but not too strong and in too close proximity to impede the desorption of acrylic acid in the gas phase.

Conclusions

Several bifunctional catalysts were studied with the aim of finding molecular-level relations that link their structures to the respective catalytic behavior for the oxidehydration of glycerol into acrylic acid. Indeed, despite the fact that all catalysts presented acid properties to efficiently dehydrate glycerol into acrolein with vanadium as the only redox element, their catalytic performance as a function of temperature and partial pressures of reactants was remarkably different. A tangled scheme emerged, in which several physicochemical properties of the catalysts (derived from their different structures) were found to govern the three main elementary steps responsible for the catalytic phenomenon: adsorption, surface reactions, and desorption. Remarkably, the same surface features played different roles in the multiple steps required to produce acrylic acid from glycerol, that is, its dehydration into acrolein and the partial oxidation of the latter into the acid monomer. This work is the first example of a systematic study that aimed to find structure-reactivity correlations for a broad variety of vanadium-containing catalysts for the one-pot oxidehydration of glycerol into acrylic acid. It revealed the role played by the different physicochemical features of the catalysts and their influence on the overall catalytic performance, and it suggested several key features to pursue for the development of new catalysts.

Experimental Section

Catalyst preparation

Details about the preparation of the catalysts are reported in the Supporting Information. In short, pure hexagonal tungsten oxide (sample WO_x) and a hexagonal-tungsten/vanadium oxide (sample WV) were prepared following a previously reported procedure.^[14] Untreated WO_x and WV, that is, fresh samples still containing ammonium ions in the hexagonal channels, were used as the starting materials for ion exchange. Indeed, it is known that the ions present in the hexagonal channels (e.g., NH₄⁺) of tungsten bronzes can be exchanged with other cations.^[58] Precisely, WO_x was exchanged with VO²⁺ ions (sample VO-WO_x). Zeotype AlPO₄-5 catalysts were prepared hydrothermally by following conventional procedures.^[38] Cobalt was also introduced during the synthesis to improve the acid properties (sample CoAPO). Vanadium was added either during the synthesis, so as to obtain in-framework vanadium species (sample VCoAPO) or by using postsynthetic incipient impregnation to create extra-framework vanadium species (VO_x/ CoAPO); particularly, VCoAPO was impregnated with an additional amount of V to obtain a catalyst with both in-framework and extra-framework V species (sample VO_x/VCoAPO). The commercial VPP catalyst used for this study was the industrial catalyst used by DuPont to produce maleic anhydride from *n*-butane; this catalyst was studied in depth by various authors.^[27] Particularly, we used its calcined form.

Catalyst characterization

IR spectroscopy studies were performed with a Bruker Vertex 70 FTIR spectrometer by using a MCT detector and acquiring at 4 cm⁻¹ resolution. An IR cell allowing in situ studies under controlled atmospheres and temperatures from 25 to 600 °C was connected to a vacuum system with gas dosing facility. For IR spectroscopy studies, the samples were pressed into self-supported wafers and treated at 300 °C in air flow (20 mLmin⁻¹) for 2 h followed by evacuation at 10 mPa at 350 °C for 1 h. After activation, the samples were cooled down to 25°C under dynamic vacuum conditions followed by adsorption of the different reactants, that is, acrolein, O₂, and/or H₂O in a molar ratio of 1:7:20. Spectra were recorded at increasing temperatures from 25 to 400 °C. At each temperature, one spectrum was recorded at the working temperature and another one after cooling down the pellet to 25 °C to favor re-adsorption of products desorbed to the gas phase. X-ray photoelectron spectra were collected by using a SPECS spectrometer equipped with a Phibos 150 MCD-9 detector and by using a monochromatic AlK $_{\alpha}$ (1486.6 eV) X-ray source and charge compensation by means of additional electron flow. Spectra were recorded by using an analyzer pass energy of 50 eV, an X-ray power of 100 W under an operating pressure of 10⁻⁴ mPa. During data processing of the XPS spectra, the binding energy (BE) values were referenced to O1s (peak settled at BE=530.5 eV) or P2p (in zeotypes, peak settled at BE = 133.5 eV). Spectra treatment was performed by using CASA software. Raman spectra were recorded at ambient temperature with a $\lambda = 514$ nm laser excitation with a Renishaw Raman spectrometer ("in via") equipped with an Olympus microscope and a CCD detector. The laser power on the sample was 15 mW and a total of 20 acquisitions were taken for each spectra. Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic $CuK_{\alpha 1}$ source operating at 40 kV and 30 mA was used. Temperature-programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 equipped with a TCD detector by using 10% H₂ in Ar as the reducing gas (total flow rate of 50 mLmin⁻¹). The temperature was varied from room temperature to 800 °C. The heating rate was maintained at 10°Cmin⁻¹. Temperature programmed desorption of ammonia mass spectrometry (NH₃-TPD-MS) experiments were performed with a TPD/2900 apparatus from Micromeritics. The sample (0.30 g) was pretreated 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 He stream for 15 min prior to increasing the temperature up to 500 °C in a helium stream of 100 mLmin⁻¹ and by using a heating rate of 10 °Cmin⁻¹. The NH₃ desorption was monitored with a thermal conductivity detector (TCD) and a mass spectrometer following the characteristic mass of ammonia at 15 amu. UV/Vis spectra were collected with a Carry 500 (Agilent) spectrometer acquiring in the $\lambda = 200-800$ nm range.

Gas-phase catalytic tests

Reactivity experiments for the aerobic transformation of glycerol were performed by using a continuous flow reactor made of glass operating at atmospheric pressure. For each condition, all the reaction parameters are listed in each figure. A catalyst amount ranging from 0.10 to 0.50 g was loaded in powder form. Residence time [calculated as the ratio between catalyst volume (mL) and total gas flow (mLs⁻¹), the latter being measured at room temperature] was varied. Inlet feed composition was also changed according to the desired compositions. If not differently specified, the catalytic results were obtained after a reaction time of 90 min. In the

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figures included within this paper, minor identified products and unknown compounds that eluted were grouped together under the heading "Others". Cyclic ethers were also sometimes produced; however, as it was not possible to perfectly resolve each peak corresponding to each cyclic ether with the chromatographic setup used, the latter compounds and the heaviest compounds not eluted in the GC column (left as residues on both catalyst surface and reactor walls) were quantified as the lack to total C balance and are labeled "Heavy compounds". More details about products analysis were previously reported.^[17,18]

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A. Chieregato, C. Bandinelli, P. Concepción, M. D. Soriano, F. Puzzo, F. Basile, F. Cavani,* J. M. L. Nieto*

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



V for victory! The nature of the V species in vanadium-containing materials affects the catalytic performance of the oxidehydration reaction of glycerol to acrylic acid. Structure-reactivity correlations are clearly behind these results. Herein, we draw conclusions on the role played by the various physicochemical features of the different oxides in terms of the adsorption, surface reactions, and desorption of the reagents and reaction products.