

A Career in Catalysis: Fabrizio Cavani

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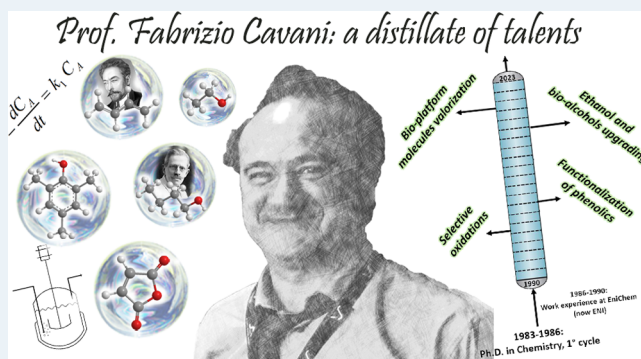
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ABSTRACT: This Account is to celebrate the 65th birthday of Fabrizio Cavani and his unique and distinguished career in catalysis, a passionate research work often performed in strong collaboration with companies and focused on both a fundamental understanding of the phenomena and possible industrial applications. The aim of this review is to provide an outline of his career and highlight some of the most important contributions he has made to the field of heterogeneous catalysis and in the development of innovative catalytic processes. The manuscript will also highlight his capacity to involve students and young researchers in his activities, stimulating scientific curiosity and passion with his speech and lectures. Indeed, Prof. Cavani was often a beacon of science and inspiration for colleagues and friends, a privileged spokesman for industrial collaborations, and a suitable guide leaving his mark as a mentor on hundreds of students who spread out his philosophy in the industrial world of chemistry.

KEYWORDS: heterogeneous catalysis, metal oxides, heteropolyacids, selective oxidations, alkylation processes, biomass valorization



1. INTRODUCTION

Prof. Fabrizio Cavani's career in catalysis started in 1983, after his degree in industrial chemistry at the University of Bologna. Since then, he has contributed to various fields in heterogeneous catalysis, dealing with many scientific interests (Figure 1). Especially, he devoted himself to develop and study various original materials and processes with a tight connection with industrial partners, leading to remarkable advancements both in the commercial application as well as in facing challenges related to the comprehension of materials' fundamentals and the discovery of unconventional reaction mechanisms. In his career, Cavani also loved to work on uncommon and "dream" reactions, devoting his great talent to increasing the understanding and better identifying new opportunities for research and applications presented by the changing scenario in the chemistry and energy sectors.

Prof. Fabrizio Cavani, born in 1958 in Modena, Italy, received his Ph.D. in 1987 at the University of Bologna. After completing his Ph.D., he was recruited by EniChem Sintesi (now ENI) in Milan to work on the R&D Center. Since the beginning of his scientific career in company, his work aimed at developing novel catalysts for industrial applications and his early research focused on alkylation of aromatics with mixed liquid/gas phase processes and oxychlorination of ethylene with processes in the gas phase. The work carried out at ENI had a significant impact on company research and led to the development of a new commercial process for the alkylation of

benzene with propylene and ethylene, marketed by Polimeri Europa, then Versalis. In 1990, Cavani, after winning an academic position at the Bologna University, decided to end his industrial career and joined the academic staff in the Faculty of Industrial Chemistry of Bologna where he is currently full professor in Industrial Chemistry. During his industrial and academic career, Cavani has published many scientific articles and contributed to several expert reviews and books in the fields of catalysis and the development of innovative and sustainable processes for industrial chemistry (Figure 2). In addition, he is author of more than 40 patents, 6 of which have reached the industrial application phase. During his work, he also contributed to domestic and international societies of catalysis being the President of the Interdivisional Group of Catalysis of the SCI, member of the Board of the Division of Industrial Chemistry of the SCI, member of the Board of EFCATS, the European Federation of Catalysis Societies. Moreover, he is a member of the Advisory Board of prestigious Journals, such as the journal "Green Chemistry" of

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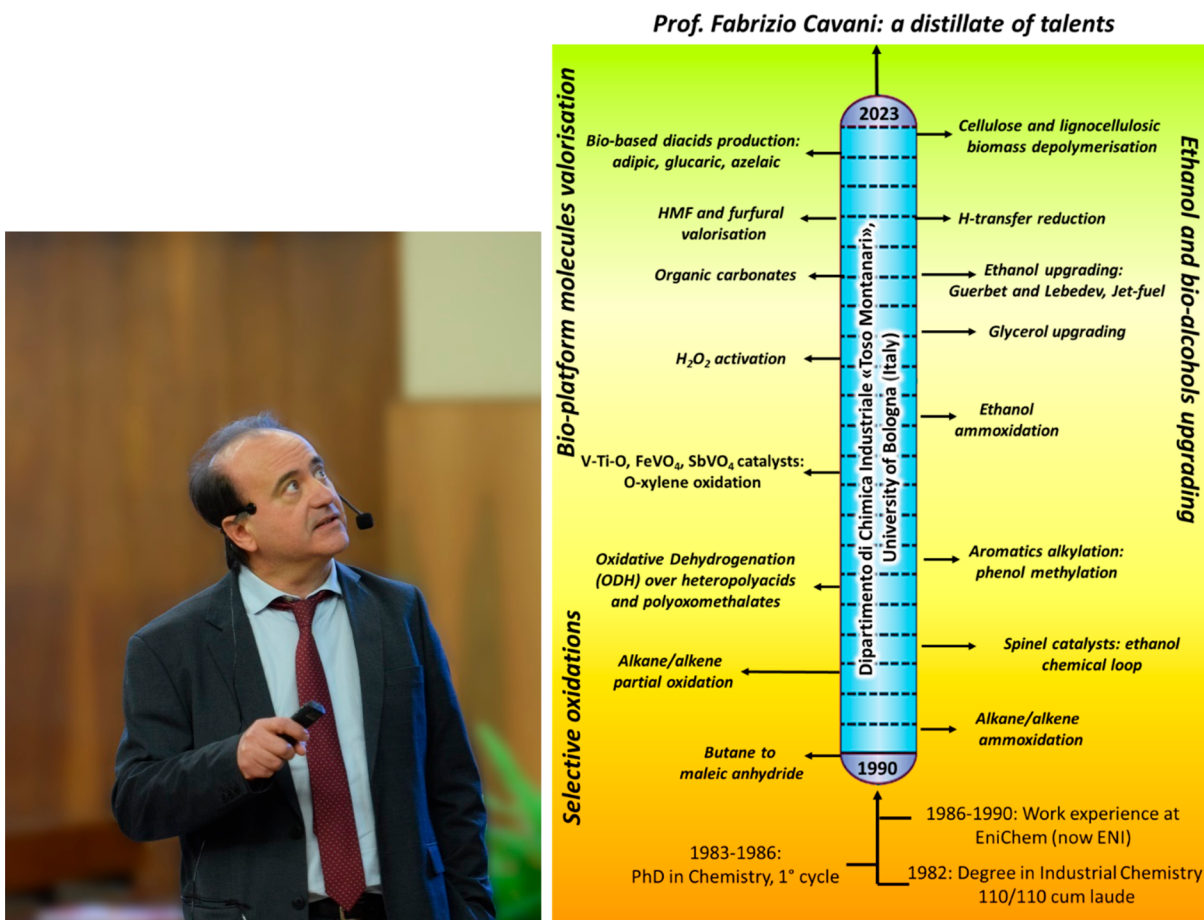


Figure 1. Fabrizio Cavani: a distillate of talents. The left-hand side shows Cavani presenting his research work during a conference; the right-hand side provides a brief recap of the main scientific interests and timeline of Cavani's career.

the RSC, and of the Editorial Board of the journal "ChemSusChem", of Wiley VCH. Thanks to his important contributions in the fields of industrial chemistry and catalysis, Cavani was awarded with the Silver Plate Paolo Chini Memorial Lecture (2012) and with the Medaglia Mario Giacomo Levi (2017) by the Division of Industrial Chemistry of the Italian Chemical Society (SCI); the latter for his pivotal contribution to the development of the maleic anhydride production process together with Polynt S.p.A company.

Behind his outstanding scientific career, Prof. Cavani is a man with an impressive personality. Capable to bewitch the audience in conference speeches and to impart his passion for industrial chemistry to the Academy of science, technicians from industry and students with the same enthusiastic engaging mode which translate his soul devoted to chemistry to every single listener. He is famous in the academic community also for his kind and friendly approach to collaborations and for his special consideration for the dissemination of suitable tools to favor the growth of young future researchers and company managers. For example, while holding the capacity of scientific community coordinator (e.g., of the interdivisional board of catalysis of the Italian chemical society and of the center of catalysis of the university of Bologna), he strongly promoted innovative events completely devoted to Ph.D. students. Being open minded to any kind of scientific and industrial interactions, he is a fruitful and pleasant company, who embellishes the atmosphere of meetings and conferences.

The following sections highlight some of the main fields in which Cavani has worked.

2. GAS-PHASE SELECTIVE OXIDATION AND AMMOXIDATION REACTIONS

The fundamental investigation on selective oxidation catalysis has always been one of the core interests of Cavani's work.¹ In the following sections, several reactions and different approaches will be described, with a special focus on the optimization of the heterogeneous catalyst active and selective toward oxidation and/or ammoxidation of selected substrates. A brief overview of the main reactions taken into consideration are reported below (Scheme 1).

2.1. Oxidation of 1-Butene and Butadiene to Maleic Anhydride. Cavani's contribution in oxidation reactions came first to a scientific audience with his Master's degree, developed under the supervision of Prof. Ferruccio Trifirò, entitled "Study of catalytic oxidation of C4 fraction to maleic anhydride with mixed oxides based on P and V". The topic of the thesis arose from a friendship of the group with an Erlangen University professor who asked Trifirò to work in Bologna in the application of a mathematical model for the optimal preparation of V/P mixed oxides (VPO catalyst). Main interest in VPO catalyst was its use in the industry for *n*-butane oxidation and the Trifirò work in the oxidation of 1-butene with a joint international collaboration.² In his thesis, Cavani highlighted the possible use of VPO as catalysts for the oxidation of 1-butene, butadiene and *n*-butane to maleic

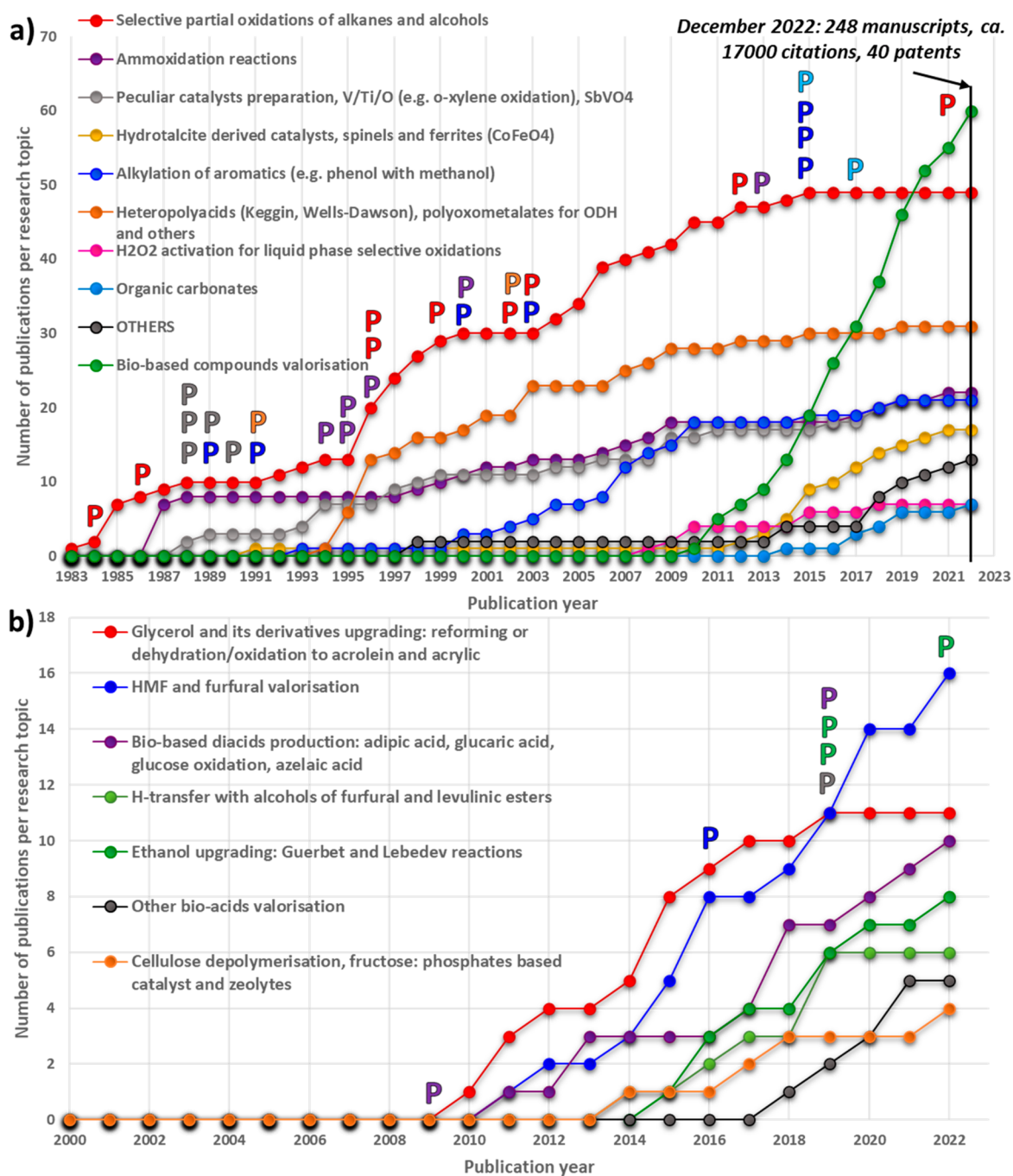


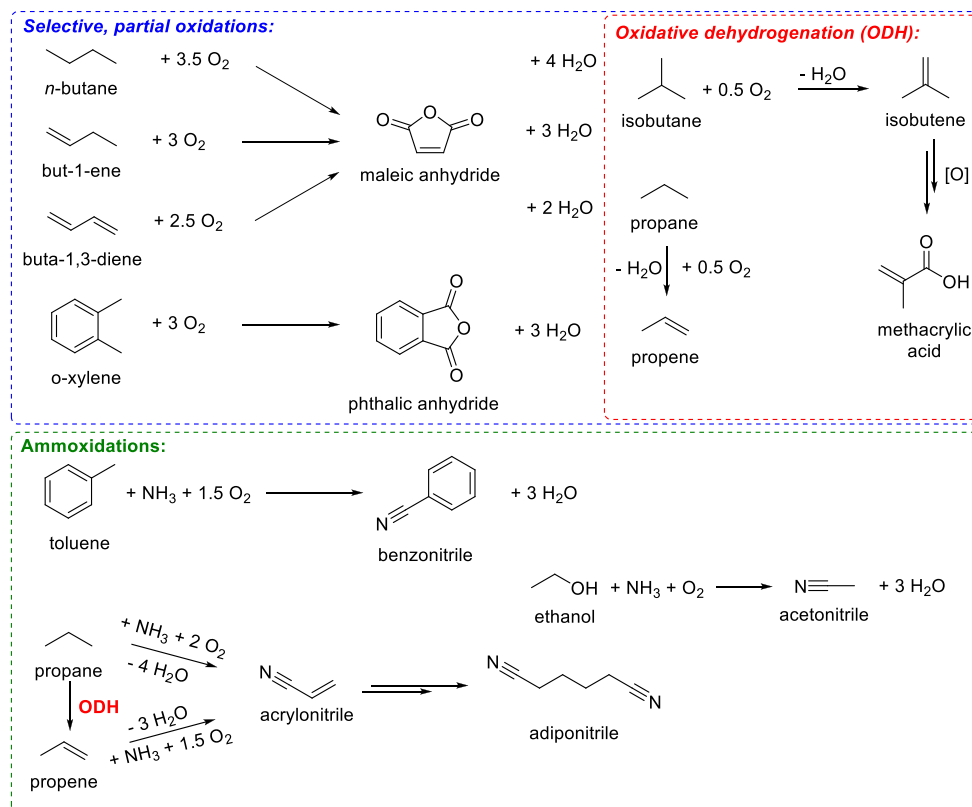
Figure 2. Cavani's research topics of interest: history and evolution. **Figure 2a:** number of publications and patents "P" filed per research topic between 1983 and 2022. **Figure 2b:** detailed subdivision of the research topics inserted in "bio-based compounds valorization" and inherent patents.

anhydride. Investigation of the kinetics of the reaction was done, and a Langmuir–Hinshelwood type model was proposed to determine the rate-determining step in the reaction between adsorbed oxygen and the intermediate butadiene adsorbed on adjacent sites.^{3,4} These studies showed the importance of operating under oxygen-enriched air conditions in order to avoid the negative effect of the reactant on the rate of maleic anhydride formation. In the following studies, Cavani demonstrated the importance to control the P/V surface atomic ratio exploring methodologies for the synthesis of VPO in organic and aqueous medium. The screening of catalytic performance for C₄ (*n*-butane and 1-butene) oxidation to maleic anhydride stated that the tuning of

the oxidation state of V and surface area of the catalyst allow controlling activity as well as selectivity toward maleic anhydride.^{5–7}

At that time, the interest in production of maleic anhydride from butane was in the early stages, becoming in the following decades one of the most important selective oxidation reactions with industrial application, thanks to the properties and the potential uses of maleic anhydride. This topic can be defined as the "youthful love" of Cavani, and he studied VPO catalyst extensively in the last 40 years, often in collaboration with Lonza Alusuisse company (now Polynt S.p.A.) as reported in section 2.6.

Scheme 1. Overview of the Main Oxidation and Ammoxidation Reactions Investigated by Cavani



2.2. Oxidation of *o*-Xylene to Phthalic Anhydride.

Cavani's Ph.D. project (1983–1986 at Trifirò's group) was devoted to the "Oxidation and ammoxidation in the vapor phase of alkyl aromatics with catalysts based on V/Ti/O", avoiding the use of toxic reagents and choosing catalysts used in the industry in the oxidation of *o*-xylene to phthalic anhydride, a reaction that became lately another subject of his research. He studied the effect of different methods, such as flash drying, coprecipitation, wet impregnation, and grafting for the preparation of mixed oxide V/Ti/O catalysts.^{8,9} Suitable characterization techniques demonstrated the importance of the *in situ* formation, presence and number of surface VO²⁺ ions in order to obtain active catalysts for the oxidation and ammoxidation of *o*-xylene and toluene, respectively. Furthermore, Cavani and co-workers investigated the positive effect of dopants (e.g., Cs, Sn and Sb) as promoters for the stabilization of the most active species, such as isolated vanadium and resulting improvement of the catalytic activity in the oxidation of *o*-xylene to phthalic anhydride. These studies finally concluded that the desorption of intermediates was facilitated and therefore maintaining a cleaner and more oxidizing catalyst surface.^{10–15} Lately, the effect of steam in the oxidation of *o*-xylene was studied by using a combination of *in situ* Raman spectroscopy and catalytic studies, showing the beneficial role of steam on catalytic activity ascribable to the higher dispersion of bulk vanadium oxide and therefore increasing the number of active sites.¹⁶ Within this field, Fabrizio established important industrial collaborations such as the strategic partnership with Lonza Alusuisse.

2.3. Ammoxidation Reactions to Produce Nitriles.

Besides selective oxidation, another main theme of Cavani's Ph.D. project was the ammoxidation of alkyl aromatics with

NH₃ and O₂, using V₂O₅ supported on TiO₂ catalysts. Indeed, the so-produced aromatic nitriles are used as intermediates and reagents in several chemical processes. Cavani focused on the investigation of the ammoxidation of toluene to benzonitrile as well as the ammoxidation of *p*-xylene, *m*-xylene, *p*-chlorotoluene, and *p*-methoxytoluene. In the case of the ammoxidation of toluene to benzonitrile, it was shown that the synthesis of efficient mixed oxide V/Ti/O catalysts was possible using contemporaneous hydrolysis and precipitation of V₂O₅ and TiO₂. By means of characterization and investigation of the catalytic performance, the presence of V⁴⁺ was found to be responsible for the toluene activation, whereas the presence of V⁵⁺ promotes the parallel undesired combustion of ammonia to nitrogen, while the presence of amorphous V₂O₅ is inactive for all the reaction steps.¹⁷ Systematic mechanistic studies for the oxidation and ammoxidation of toluene using monolayer vanadia-titania as model catalysts were also reported, revealing intermediates, such as adsorbed benzyl radical species on the catalysts' surface. Consecutive oxidation produces benzaldehyde, adsorbed benzoates, and maleic anhydride. Moreover, the coadsorption of toluene and ammonia produces adsorbed benzylamine, which is also observed as a byproduct during the reaction, and benzonitrile.¹⁸ Concerning alkyl aromatics oxidation to nitriles, for example, in the ammoxidation of toluene, *p*- and *m*-xylene and *o*-chlorotoluene, it was developed the synthesis of efficient V₂O₅/TiO₂ catalysts based on coprecipitation techniques.^{19–22} It was concluded that the main factors influencing the selectivity were the ammonia partial pressure and the amount of vanadia in the catalyst. The role of NH₃ was found to inhibit the overall reactant conversion relative to its oxidation and to stabilize the intermediate of alkylaromatic activation, avoiding further

combustion. The highest catalytic performance was obtained with the amounts of vanadia corresponding to the formation of a monolayer coverage of the anatase TiO_2 surface. Finally, kinetic and mechanistic studies of toluene ammoxidation to benzonitrile were carried out using a tubular flow stacked pellet reactor and V/Ti/O catalysts. It was demonstrated that the slow step of the reaction is the initial reaction of activated toluene on the surface of the catalyst. Nevertheless, the reactions of benzonitrile and carbon dioxide formation depend on the hydrocarbon partial pressure (Langmuir–Hinshelwood dependence) and are independent respect to the oxygen partial pressure when this is in large excess with respect to the stoichiometric amount. An inhibition effect by ammonia on the global conversion of toluene was observed and ascribed to a competition between the hydrocarbon and ammonia for the same kind of active sites.²³

Ammoxidation has also been exploited with propane as an alternative feedstock for the production of acrylonitrile previously produced from propylene, which already represented a sustainable alternative compared to the traditional acetylene and HCN process. The main advantage resides in the fact that propane is cheaper than propylene as being an impurity of crude oil or natural gas. In collaboration with Prof. Robert Grasselli and lately with the French Rhone Poulenc (later Rhodia) company,²⁴ the group of Bologna proposed the synthesis of acrylonitrile with a plethora of ammoxidation catalysts.^{25,26} Cr/Sb mixed oxides (Cr/Sb/O) with a rutile-type structure showed that whereas the selectivity increased with increasing Sb content, the catalytic activity rose with higher Cr/Sb ratios. Sb-enriched rutile-type structure in the outmost layers and the ability to host excess of antimony in the structure were the main factors to determine the catalytic performance, and make it much less sensitive to the presence of extra-rutile antimony oxide.²⁷ Rutile-type Cr/V/Sb mixed oxides, catalysts for the ammoxidation of propane to acrylonitrile, were useful to demonstrate that for atomic ratios Cr/V/Sb = 1/x/1 and 1/x/2, the systems were monophasic. The nature of the V ion was a function of the atomic ratio (Cr + V)/Sb. For samples having a ratio between 0.5 and ≈ 1 , the V^{3+} ion was the prevailing species, while for samples having atomic ratios higher than ≈ 1 and lower than 2 both V^{3+} and V^{4+} species were identified. Moreover, the relationship with analogous rutile systems, i.e. Fe/V/Sb/O and V/Sb/O, was studied, and a general model was developed which justifies the possible formation of different V valence states in function of the atomic ratio between components.^{28,29} Monophasic, rutile-type Mo/V/Sb mixed oxides highlighted that the addition of Mo increased the catalytic activity in propane ammoxidation, but the catalysts became less selective to acrylonitrile, due to the increased contribution of combustion, and more active in ammonia oxidation to molecular nitrogen. This was attributed to an enhanced Lewis acidity, which increased the interaction of the catalyst with ammonia and favored its unselective transformation. The introduction of Mo in the rutile lattice did not provide the development of allylic (amm)oxidation sites, but rather generated species characterized by an increased affinity for ammonia, and by a preferential transformation of the latter into nitrogen.³⁰ In rutile-type Cr/V/Sb/Nb mixed oxides, increasing amounts of Nb to the rutile Cr/V antimonate led to a considerable increase in the selectivity to acrylonitrile and to a lower selectivity to N_2 derived from ammonia overoxidation only when excess Sb was present with respect to the stoichiometric requirement for the formation of

the rutile compound. The multicomponent rutile had a highly defective structure with cationic vacancies in relation to excess Sb^{5+} with respect to the stoichiometric composition. The progressive increase in Nb concentration in this mixed oxide with increasing Nb loading led to a partial segregation of Sb oxide in the form of Sb_2O_4 . The excess Sb in rutile provided the active sites for allylic ammoxidation on intermediate adsorbed propylene. The contemporaneous presence of Nb in the lattice improved the efficiency of these sites and was responsible for the better catalytic performance with respect to the Cr/V/Sb/O systems.³¹ In rutile-type Cr/Nb and V/Nb mixed oxides, graphite-like carbon deposits build up during calcinations in an inert atmosphere. Their decomposition provided the reducing agent that led to the formation of rutile VNbO_4 at relatively mild conditions. The synthesized catalysts were tested for the ammoxidation of propane under both hydrocarbon-rich and hydrocarbon-lean conditions. Catalysts were active but nonselective to acrylonitrile. The catalyst modifications occurring during the reaction were followed by operando Raman–GC methodology. It was found that VNbO_4 transforms into a catalyst active and selective for acetonitrile under leaner hydrocarbon feed. CrNbO_4 and VNbO_4 rutile phases require different conditions to be formed. Unlike CrNbO_4 , the formation of VNbO_4 was strongly dependent on the conditions, being decomposed in an oxidizing environment. The new catalytic system was significantly more active, but essentially more selective for acetonitrile formation.³²

For rutile-type V/Sb mixed oxide, the use of a mechanochemical synthetic method allowed smaller crystallite size of vanadium antimonate characterized by a higher concentration of cationic defects than the catalyst prepared by coprecipitation. This led to a considerably higher activity in propane ammoxidation but to a lower selectivity to acrylonitrile.³³

The effect of the composition of rutile-type Sn/V/Nb/Sb mixed oxide catalysts on the catalytic performance in the gas-phase ammoxidation of propane to acrylonitrile disclosed that by a systematic variation in the atomic ratio between components, the control of activity and selectivity was evident. Sb generates mixed oxides containing specific sites for the allylic ammoxidation of propylene, and Nb enhanced their activity and selectivity. However, when a large amount of Nb is present, the presence of Nb_2O_5 decreases the selectivity to acrylonitrile. In general, Sn/V/Nb/Sb/O are efficient catalysts for the ammoxidation of propane to acrylonitrile under hydrocarbon-rich conditions due to the fact that (i) these samples have a significant increase of specific surface area ranging between 60 and 70 $\text{m}^2 \text{g}^{-1}$; (ii) tin oxide incorporates Sb cations and provides the rutile matrix for the dispersion of the active components.^{34,35}

Looking at the effect of Ga, a new class of rutile-type GaSbO_4 -based multicomponent oxides were investigated. GaSbO_4 rutile was much less active than the conventional VSbO_4 -based rutile systems and showed good selectivity to acrylonitrile. The role of V was investigated by the incorporation of V in GaSbO_4 with an improvement in the catalytic activity and a decreased maximum selectivity to acrylonitrile. Better catalytic activity and selectivity to acrylonitrile was thus achieved by the incorporation of Nb and thereby developing a Ga/V/Nb/Sb mixed oxide.³⁶

Lastly, in more recent years, the ammoxidation of bioethanol was in depth investigated by Cavani's group leading to some fundamental understanding not only on the mechanism but

also on process design and Life Cycle Assessments (LCA) investigations.^{37–39}

2.4. Oxidative Dehydrogenation (ODH) of Light Alkanes. Light olefins (ethylene, propylene, butenes, and isobutene) are currently produced almost entirely by steam cracking of petroleum fractions, and some are produced by dehydrogenation of the alkanes. Within the framework of the long-lasting collaboration with Eni, Cavani started his research on the production of olefins from light paraffins (impurities of natural gas) by oxidative dehydrogenation (ODH), a process with lower energy costs and an alternative to the dehydrogenation already used in the chemical industry. The research started with an industrial sponsorship by Eniricerche giving rise to the publication of an important review in the topic of oxidative dehydrogenation of alkanes.⁴⁰ Lately, another outcome of his industrial research collaborations, with Snamprogetti, led to a publication on the synthesis of isobutene by oxidative dehydrogenation of isobutane.⁴¹ At the side of research developed with the industry, Cavani engaged in several academic collaborations: with the University of Udine and R.G. Finke (USA) working on the oxidative dehydrogenation of isobutane to isobutene, and with the University of Genova on the ODH of propane to propylene using membrane.⁴² Crossing the boundaries in his collaborations with chemical industries, Cavani also started a study on the catalytic selective oxidation of isobutane to methacrylic acid with E. Etienne, from Elf Atochem, a French company. Other reactions of interest that Cavani introduced in his research business within this field are represented by (i) dehydrogenation of isobutane to isobutene; (ii) the consecutive oxidation of isobutene to methacrylic acid; (iii) the oxidative dehydrogenation of propane to propylene under a renewed collaboration with Eni and Snamprogetti;⁴³ and (iv) the oxidative dehydrogenation of isobutyric acid to methacrylic acid.⁴⁴

Along the same period of his career, Cavani published two important reviews on the topic of the ODH of light alkanes to olefins.^{45,46} In the case of the dehydrogenation of ethane to ethylene, the catalyst of choice was initially based on tin–vanadium mixed oxides. The structure–activity correlation showed that the formation of $V_xSn_{1-x}O_2$ can lead to improved stability of the structure with x value lower than 0.02. Furthermore, the presence of V^{4+} is an essential factor for improved selectivity to ethylene at a reaction temperature above 480 °C.⁴⁷ A subsequent field of interest of Cavani and co-workers regarded the catalytic performance of heteropoly compounds, with a focus on the modification of potassium/ammonium salts of 12-molybdophosphoric acid with antimony for improving thermal stability without structural decomposition at temperatures up to 540 °C. Further modification of the catalysts by the addition of small amounts of iron, chromium, tungsten, and cerium ions led to an improvement of the catalytic performance.^{48–50}

The oxidative dehydrogenation of propane to propylene was investigated using a γ - Al_2O_3 supported vanadium oxide catalyst. It was shown that when the V_2O_5/γ - Al_2O_3 was coated in the form of a thin layer over a cylindrical ceramic support using a monolith-type reactor configuration, a considerable enhancement of the catalytic performance was achieved, because the consecutive reaction of propylene overoxidation, responsible for a remarkable decrease in selectivity at high conversions in packed-bed reactors, was minimized.⁵¹ In

another study, the use of efficient V/Nb mixed oxides for the ODH of propane to propylene was demonstrated.

The reactivity tests were carried out under cofeed and under redox-decoupling conditions, with alternate-feeds of propane and air using a cyclic operation. In the latter case, a higher selectivity to propylene is achievable operating at low propane conversion. This was attributed to a proposed reaction mechanism mainly involving propane dehydrogenation rather than the ODH, occurring on the reduced catalysts. During prolonged contact with propane in the absence of molecular oxygen, the low valence state of V was developed.⁵²

Vanadium oxide on different supports, namely, alumina, titania, titania–alumina cogel, and silica, were tested in the reaction of propane ODH to propylene under cofeed and under redox-decoupling conditions (i.e., by alternating the reducing and the reoxidation steps). Under cyclic conditions, a higher selectivity to propylene was ascribable to a dehydrogenative mechanism. On the contrary, the oxidative mechanism is favored by oxidized catalysts with a conversion higher than 20% even in the absence of molecular oxygen. Moreover, Cavani discovered that vanadium oxide catalysts either dispersed inside a high-surface-area silica gel, or supported over silica, not only allowed higher propane conversions than catalysts in which vanadium oxide was deposited over alumina or titania, but also gave the higher enhancement of selectivity to propylene with respect to the cofeed conditions. This behavior is likely due to the nature of the vanadium species developed on silica support.⁵³

The influence of the methodology for VO_x -based catalysts was investigated by preparing these catalysts by flame pyrolysis (FP). In the case of the ODH of propane to propylene, these catalysts were shown to be more selective and to have a higher dispersion of V in the sample bulk than those prepared by impregnation. Furthermore, catalysts prepared by the same method were less active, but more selective when VO_x was supported on SiO_2 instead of Al_2O_3 . Mechanistic studies by means of EPR spectroscopy showed the presence of isolated, tetragonally distorted paramagnetic complexes of V^{4+} forming a monolayer on the sample surface with a strong out-of-plane V^{4+} –O bond. EPR analysis, being sensitive to the detection of V^{4+} sites, was employed as a powerful tool to elucidate the local structure of the active sites and their affinity toward oxygen in an indirect way and to correlate with the catalytic performance of the V-based catalysts, allowing to draw reliable previsions. It was concluded that this phenomenon can be correlated to catalytic activity and to selectivity to propylene, the former property increasing and the latter decreasing with increasing the contribution of segregated V .⁵⁴

Cavani's research on flame pyrolysis exploited several characterization techniques, i.e., TEM, XAFS, XPS, and IR, to better characterize thoroughly the local structure of V active sites depending on both the support type and the preparation method. Indeed, the presence of dispersed monovanadate species was shown to be responsible for the increased selectivity to propylene. Moreover, only with the flame pyrolysis method it was possible to obtain silica and alumina supported V-based catalysts with high dispersion of V at relatively high loading. Moreover, V dispersion also showed an interesting correlation with surface acidity and V oxidation state, at least for the silica-supported samples, which in turn could explain the observed selectivity trend.⁵⁵

In the case of the oxidative dehydrogenation of isobutane to isobutene, Cavani and co-workers investigated the synthesis of

CeO₂–ZrO₂ mixed oxides. It was reported that the formation of a homogeneous, fluorite-type solid solution with a high degree of reducibility and capacity of oxygen uptake compared to pure CeO₂ is responsible for the enhanced selectivity to isobutene.

This enhancement was mainly attributed to an increased oxygen mobility and an increased activity for the Ce⁴⁺/Ce³⁺ redox couple, occurring as a consequence of the creation of surface and bulk defects in the solid solution, induced by the introduction of the smaller Zr⁴⁺ cation in the fluorite lattice. They demonstrated that modifying the lattice oxygen mobility and the kinetics of Ce⁴⁺/Ce³⁺ reduction by introduction of isovalent elements could represent an important new tool for the design of efficient and stable oxidation catalysts.⁵⁶

In the following studies, the thermal stabilities of the Wells–Dawson heteropoly compounds (K₆P₂W₁₈O₆₂) were examined under both reducing and oxidizing conditions, and their structural and morphological evolution were characterized by several complementary characterization techniques. It was shown that the primary structure of this compound remained intact up to 770 K, while at higher temperature, structural changes and rearrangements were observed. The best catalytic performance was shown by the rearranged Wells–Dawson compound.

Based on the characterization of the materials, it was concluded that these compounds have a low tendency to exchange oxygen at the desired reaction temperature at which the reaction is carried out. Moreover, taking into account that the choice of the reaction mixture was quite reducible (high hydrocarbon-to-oxygen ratio) indicated that the working catalyst might be in a reduced, heteropolyblue form.⁵⁷ The thermal and structural stability of the previously reported Wells–Dawson-type heteropoly compound was lately examined by means of several characterization techniques. It was found that calcination at temperatures higher than 850 K led to the formation of a Keggin-type compound “K₃PW₁₂O₄₀” which showed a higher activity in the selective oxidative dehydrogenation of isobutane to isobutene compared to both the Wells–Dawson precursor and to pure, authentic K₃PW₁₂O₄₀. This was one of the first reports showing that a high temperature rearrangement could produce an active and amorphous surface layer, which is more efficient as a catalyst for the isobutane oxidation than the precursor K₆P₂W₁₈O₆₂.⁵⁸

Dawson-type stable heteropolycompounds K_xP₂W₁₇MO_{62–y}·*n*H₂O (with *y* = 0 when M = W and *y* = 1 when M = Fe, Mn, Co, Cu), for the oxidehydrogenation of isobutane were also field of interest for Cavani et al. They showed that the incorporation of Fe led to the highest catalytic activity, but only by a factor of 1.2 versus the parent K₆P₂W₁₈O₆₂. The enhanced activity was attributed due to the presence of additional possible active sites, including (i) Fe–O–W, (ii) adsorbed oxygen species, Fe–OO· or Fe–O· and W⁵⁺.⁵⁹

Cavani and co-workers also examined the thermal stability of Wells–Dawson polyoxometalates and their catalytic properties in isobutane ODH as a function of several parameters, such as temperature, isobutane, oxygen content, and the presence of steam. It was shown that the lacunary K₁₀P₂W₁₇O₆₁ and the iron-substituted K₇P₂W₁₇FeO₆₁ were stable under oxidizing conditions up to 500 °C. At higher temperature, structural modifications were found with decomposition of the polyanion framework and formation of K/W/O and K/P/O-containing phases. Reduced Wells–Dawson compounds were active and selective to isobutene due to the possible generation of radical

species which propagated into the gas phase, thus yielding a reactivity typical of heterogeneously initiated, homogeneous reactions when the temperature was higher than 450 °C, high isobutane and oxygen concentration in the feed, and with a yield of isobutene up to 11%.⁶⁰

2.5. Oxidation of Isobutane to Methacrolein and Methacrylic Acid. Methacrylic acid is synthesized in a large majority using toxic HCN, through the formation of acetone cyanohydrin and after other two reactions. The group of Catalysis in Bologna together with the French industry Elf Atochem investigated the alternative greener process on the synthesis of methacrylic acid by direct oxidation of isobutane or from isobutene as an alternative greener environmental approach.

The oxidation of isobutane to methacrolein and methacrylic acid was carried out over potassium/ammonium salts of 12-molybdophosphoric acid (Keggin-type heteropoly compounds), with overall selectivity to the desired products being higher than 50%. The addition of iron to the catalyst's composition led to a substantial enhancement of the catalytic activity, with an increase in the yield of the desired products, even though the selectivity decreased. The enhancement of the catalytic activity was due to the substantial increase in the catalyst Lewis acidity, which could play a role in the activation of the paraffin, whereas the pathway leading to the formation of methacrolein was not substantially affected by the addition of iron. On the contrary, the route to the methacrylic acid was remarkably affected by the addition of iron. It was concluded that the acidic properties induced by iron, in terms of both Brønsted and Lewis acidity, affect the rate of methacrylic acid formation as well as the overall conversion of the isobutane. It was hypothesized that the modification of the acidic properties of the sites responsible for the formation of the methacrylic acid favors the rapid desorption of the latter, thus avoiding its overoxidation to carbon oxides.⁶¹

Spectroscopic studies proposed that the activation of the isobutane at the tertiary C–H bond could lead to the formation of an alkoxy species, which could be then converted to an allylic alkoxy species, precursor for the formation of methacrolein and methacrylic acid, and the main competitive pathways were the formation of acetic acid, maleic anhydride, and carbon oxides.

In the following studies, the effect of the molar ratio of isobutane to oxygen was investigated using as a reference catalyst ammonium salt of 12-molybdophosphoric acid (POM). The POM catalyst was found to operate with higher selectivity at isobutane-rich conditions (26% isobutane, 13% oxygen) than at isobutane-lean conditions (1% isobutane, 13% oxygen). This was attributed to the development of a more favorable distribution of reduced Mo⁵⁺ and oxidized Mo⁶⁺ sites in the POM in the former case, due to modifications occurring in the catalyst during time-on-stream at different reaction conditions.

On the contrary, strongly oxidized catalysts, like those operating under isobutane-lean conditions, are less selective, and mainly increase the yield to carbon oxides.^{62,63}

With the addition of Sb on ammonium salt of 12-molybdophosphoric acid, it was found that a decrease in the oxidation state of molybdenum could happen due to the electron exchange occurring between Sb³⁺ and Mo⁶⁺ during the calcination treatment. This reduced state for molybdenum in the POM was found to be stable even under oxidizing conditions during the catalytic process. For example, under

isobutane-lean conditions (i.e., 1% isobutane, 13% oxygen), the Sb-doped catalyst reached a selectivity as high as 40–45% to methacrylic acid.⁶⁴

Heterogeneous catalysts for the oxidation of isobutane to methacrylic acid were prepared by precipitation of ammonium salts of P/Mo polyoxometalates (POMs) by variation of the pH and thermal treatment. Depending on the pH of precipitation, different types of POMs were obtained (Keggin-type and lacunary-type) and were prepared. Their calcination, however, gave rise in all cases to a Keggin-type POM, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$. It was proposed that the generation of the active sites was a consequence of the incipient structural decomposition of the POM and migration of Mo from the Keggin anion into the cationic position of the framework either during the calcination treatment of the lacunary precursor or during the equilibration stage under reaction conditions, and these sites were responsible for the improvement in selectivity during catalyst equilibration.^{65,66}

An alternative method to develop a partially reduced compound was by the preparation of a Sb^{3+} -doped polyoxometalate using a solid-state redox reaction between Sb^{3+} and Mo^{6+} during the calcination of the polyoxometalate precursor. With this procedure, a catalyst was obtained, which did not require the preliminary equilibration, and which therefore was active and selective from the beginning of its reaction time and with enhancement of catalytic activity even under isobutane-lean conditions.⁶⁷

Iron-doped, ammonium/potassium salts of 12-molybdophosphoric acid (Keggin-type polyoxometalates (POMs) were prepared, characterized, and tested as catalysts for the selective oxidation of isobutane to methacrylic acid. Iron was present as a partly hydrolyzed species, i.e., $\text{Fe}(\text{OH})_2^+$, and excess iron was dispersed in the form of amorphous oxide or phosphate. It was found that the catalytic performance of these compounds was greatly affected by the presence of extra-framework molybdenum and iron affected by calcination treatment and the activity of Fe-containing samples increased by increasing Fe contents. However, an undesired effect was the decrease of the selectivity to methacrylic acid with an increase of Fe content.⁶⁸

In the following studies, Keggin-type P/Mo polyoxometalates (POM) were dispersed in a high-surface-area silica gel by using a cogelation procedure. The aim was the dilution of the active phase, in order to favor the dispersion of the considerable reaction heat and limit the oxidative degradation of the desired products. However, the diluted heteropolyacid was less stable than the undiluted one because of the exchange between P and Si as the heteroatom. To resolve the issue of the thermal stability, the gel was prepared in the presence of tetrapropylammonium hydroxide, and the thermal decomposition of the latter generated the ammonium ion that replaced protons in the cationic position of the POM. This enhanced the structural stability of the diluted POM but without improvement of the catalytic performance. It was hypothesized that this was due to several effects: (a) a considerable degree of combustion over methacrylic acid, (b) a modification of the redox properties of the POM as a consequence of the dilution in silica, and (c) a decreased structural stability of the POM.⁶⁹ Finally in 2018, a review article was presented by Cavani and co-workers discussing catalysts and their role in the development of clean processes and technologies for methyl methacrylate (MMA) a specialty monomer for poly methyl methacrylate (PMMA) production.⁷⁰

2.6. VPO Catalyst for *n*-Butane Oxidation to Maleic Anhydride. Maleic anhydride (MA) is a very versatile molecule because of its three different active sites featuring its molecular structure (two carboxylic groups and one double C=C bond). It is an excellent material for several types of reactions, including alkylation, polycondensation, polyaddition, and Diels–Alder reaction.

In particular, MA is an important monomer for the manufacturing of unsaturated polyester resins (used for the production of thermosetting plastics) and alkyd resins (employed as ligands in the coating industry). Furthermore, it can be used as a building block for the production of fine chemicals: for instance, by selective hydrogenation MA can be transformed into succinic anhydride or can be used as a raw material for the synthesis of γ -butyrolactone (GBL), tetrahydrofuran (THF) and 1,4-butanediol (BDO). MA also has applications in the food industries, as a precursor of malic acid and fumaric acid, both used as additives to adjust the acidic flavor. Finally, it is also used for the production of aspartic acid, precursor for the synthesis of aspartame.⁷¹

Approximately 50% of global capacity is used to produce unsaturated polyester resins, while approximately 20% is used in the alkyd resins sector. The residual is generally used as a building block/raw material for the production of all of the other chemicals.

The industrial production of MA consists of a gas phase selective oxidation of petrochemical-based feedstocks such as benzene or *n*-butane. In 2020, the yearly global capacity was approximately 3.0 million tons of MA, which is expected to increase to 4.0 million tons by the end of 2030. This growth is especially related to the expected increase in consumption of BDO-based biodegradable polymers (e.g., polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT)).⁷²

The very old technology is based on benzene selective oxidation in a multitubular fixed bed reactor using a mixed vanadium (V_2O_5) and molybdenum (MoO_3) oxide supported on an inert material as catalyst.⁷³ The production from *n*-C4 has been successful since the early 70s, enabling the progressive replacement of benzene-based plants until approximately 80% of the capacity uses *n*-C4 as a raw material.

The use of *n*-C4 instead of benzene as a feedstock for MA production has many advantages:

- (i) Lower cost: *n*-C4 is a fraction of natural gas and it is also produced by oil steam cracking.
- (ii) Better atomic efficiency: benzene is made of six carbon atoms while MA has only four, implying that there is an intrinsic loss of two carbon atoms as CO_2 . Starting from *n*-C4, the carbon content is equal, and the emission of carbon oxides is lower.
- (iii) Lower environmental impact: benzene is classified as a carcinogenic substance.
- (iv) Better MA quality due to the reduction of byproducts.

The key factor for the success of this technology has been the development of the right catalyst: a vanadium–phosphorus mixed oxide with a particular crystalline structure, vanadylpyrophosphate (VPO), which is still the only option available at an industrial scale for both developed technologies, fixed bed as well as fluid bed.

VPO has been studied extensively in the last 40 years. The rising interest for this material is clearly explained by the graph in Figure 3, which reports the yearly publications as well as the

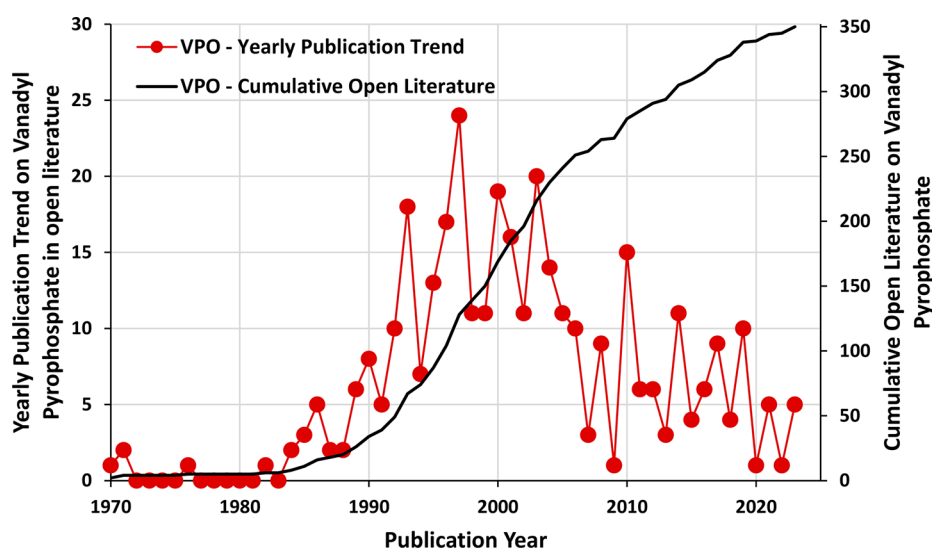
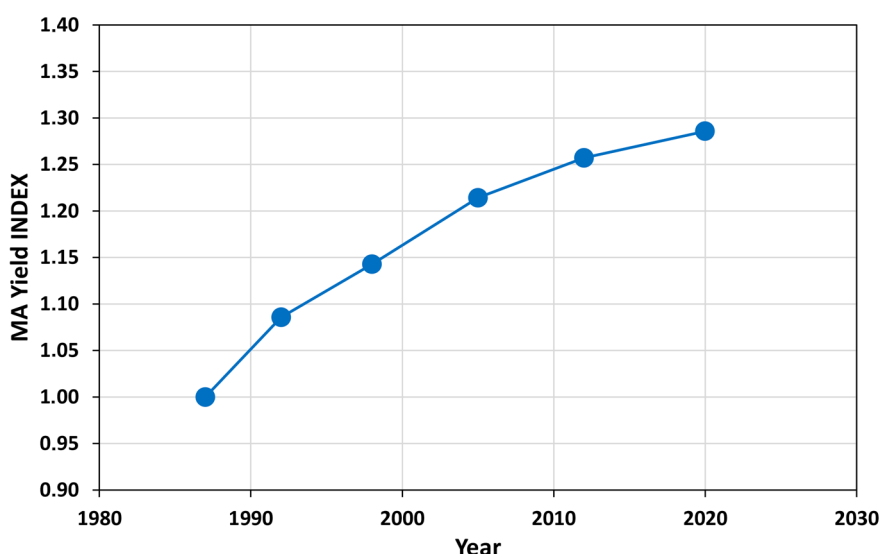


Figure 3. Vanadyl pyrophosphate (VPO) yearly publication and cumulative open literature.



1st Generation
1987

2nd Generation
1994

3rd Generation
1998

4th Generation
2005

5th Generation
2012

6th Generation
2020

Figure 4. ALMA Catalyst MA yield INDEX of the different generations developed.

cumulative open literature regarding vanadyl pyrophosphate. The history of heterogeneous catalysts goes back to the early 80s of the 20th century, as Cavani's research in catalysis, having its high-wave period in the 90s and first decade of the 21st century. More than 350 papers have been published on the topic, and Cavani is now the world leading author representing the milestone of this research field.

In the 1980s, Polynt S.p.A. (formerly Alusuisse Lonza), following the development of its own vanadyl pyrophosphate fixed-bed catalyst and a MA recovery solvent together with CBI (formerly ABB Lummus, an engineering company expert in fluid bed technology), jointly developed and successfully licensed a fluid-bed catalyst and technology named ALMA (acronym for Alusuisse Lummus Maleic Anhydride). Beginning in 1992, this joint development started one of the longest collaborations in the history of Industry and Academia. This is

when the Research Group of Cavani and Polynt, a partnership that is still in place after more than 30 years, developed the VPO catalyst for application in the ALMA fluid bed reactor with the goal of improving and enhancing the performance of Polynt's ALMA catalyst.

The collaboration has been positive throughout its history and has provided outstanding results given the nine Ph.D. theses submitted, more than 20 theses submitted for Master's degrees, 10 patents granted or currently in the application phase, more than 55 open literature articles published, and approximately 40 communications at scientific congresses.

Cavani and Polynt have focused their attention, as have most of the research groups and companies investigating the topic of VPO, on the main parameters and features affecting the catalytic performance of this material such as the P/V ratio, the crystallinity, the average oxidation state, and the presence of

dopants. A variation of these characteristics can be induced by modifying and acting on the VPO synthesis method, which involves the following steps:

- 1 Synthesis of vanadyl hydrogen-phosphate hemihydrate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, VHP) precursor starting from vanadium pentoxide V_2O_5 and phosphoric acid depends on the nature of the reducing agent used, with three different routes to be identified. VPO's final characteristics, such as P/V ratio, crystallinity and dopants can be directly tuned and modified at this stage.⁷⁴
- 2 Thermal decomposition of the hemihydrate vanadyl acid orthophosphate with total or partial loss of crystallization water is crucial. The transformation of precursor into VPO depends on multiple parameters, e.g., temperature, time and atmosphere of treatment; precursor crystallinity and morphology; P/V ratio; presence of additives or structural defects. The studies have showed that vanadyl pyrophosphate retains the morphology of the precursor: a topotactic transformation occurs during a structural conversion in which V–O and P–O bonds remain unaltered, while weak V– H_2O and P– H_2O are broken. After the dehydration of the precursor, rearrangement of the structure takes place, and finally layers of precursor condense to obtain the structure of the vanadyl pyrophosphate.^{75–77}
- 3 Catalyst shaping to give the best mechanical resistance for each type of reactor (fixed or fluid).
- 4 Catalyst activation to maximize and stabilize the catalytic performances.

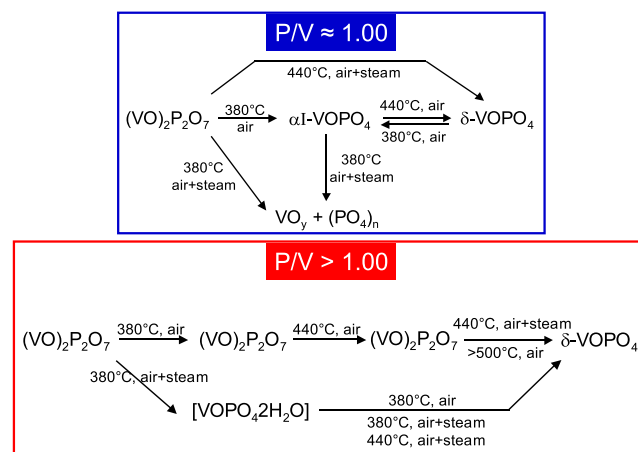
All the efforts made during the lengthy collaboration have been fruitful considering the impressive and outstanding results obtained in terms of ALMA catalyst performance improvement. Figure 4 shows the ALMA catalyst MA yield index, which is representative of the enhancement resulting from the different modifications applied to the industrial catalyst from one generation to the other. The ALMA catalyst is now in its fifth generation, and the improvement of approximately 25% of its original performance is an impressive result, especially for an industrial process.

The main changes to the catalyst production process for each new generation and the scientific findings explaining the obtained improvement are summarized here below:

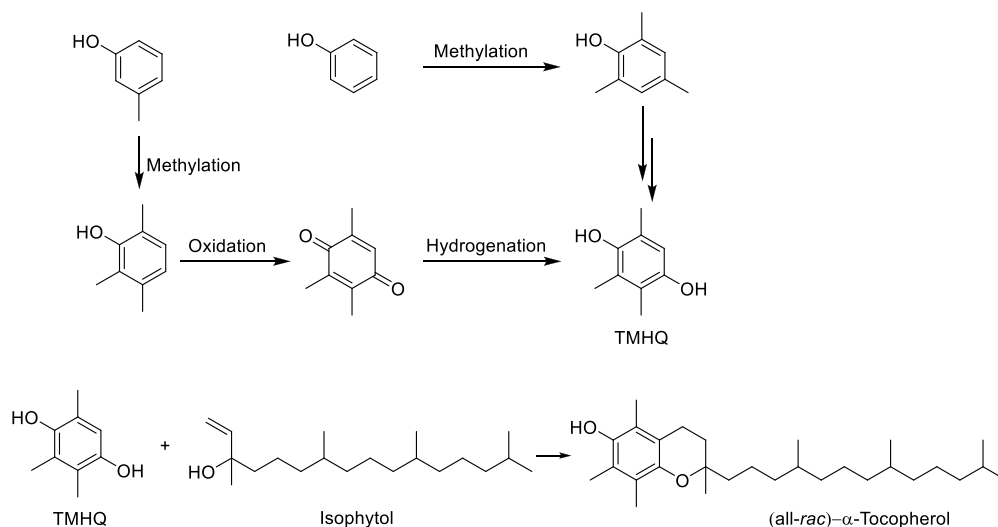
- The development of the second-generation ALMA catalyst was the result of fine-tuning the activation procedure used to promote the transformation of the hemihydrate vanadyl acid orthophosphate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (VHP) to vanadyl pyrophosphate. The original activation protocol was performed in N_2 with the temperature between 350 and 450 °C. On the contrary, the new activation was based on hydrothermal-like conditions which involved the feeding of an air/steam mixture with the proper relative ratio at a temperature range between 350 and 450 °C. The resulting activated VPO catalyst was characterized by improved crystallinity as well as an optimal average oxidation state that turned into an industrial catalyst with improved stability at the increasing time on stream.^{78,79}
- The third generation was developed by modifying the initial reaction step to obtain the hemihydrate vanadyl acid orthophosphate $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (VHP). The original synthesis was developed on the milestone of the

VPO route using iso-butanol as an organic reducing agent and reaction solvent. The new synthesis protocol was modified by adding an organic cosolvent such as benzyl alcohol, pentanediol, butanediol, and others. The addition of an organic cosolvent, particularly a glycol, resulted in a layered crystalline precursor structure with organic residues within the different planes. The presence of those structures was proven to be crucial for the production of a more active and selective VPO catalyst; the removal of these intercalated organic deposits during the final activation step was indeed responsible for the formation of a catalyst surface featured by a higher defectivity.⁸⁰ P/V atomic ratio was the second parameter studied to optimize the third-generation ALMA catalyst leading to an improved industrial catalyst featuring a specific chemical composition with an exceeding amount of phosphorus in respect to the stoichiometric. Two families of VPO catalyst, the first featured by a stoichiometric P/V ratio ($\text{P}/\text{V} \approx 1$) and the second characterized by an excess of phosphorus ($\text{P}/\text{V} > 1.00$), were intensely studied by means of steady-state reactivity tests, transient reactivity tests after *in situ* treatments and characterized by *in situ* and operando Raman and XPS spectroscopy, indicating that small differences in the P/V ratio can directly and widely affect the catalyst performance both in terms of activity and selectivity. This is the result of an active VPO superficial layer that develops differently on the base of this composition parameter. In particular, the catalyst with an excess of phosphorus ($\text{P}/\text{V} > 1.00$) was recognized as a better catalyst. Scheme 2 summarizes

Scheme 2. Schematics of the Influence of P/V in VPO on the Nature of the Active Layer



schematically the experimental results. The stoichiometric VPO exhibited poorer catalytic performance at a medium reaction temperature, especially in terms of MA selectivity, due to the high superficial density of unselective $\alpha\text{I-VOPO}_4$ and hydrolyzed $[\text{VO}_y + (\text{PO}_4)_n]$ domains deriving from the reversible transformation of $\delta\text{-VOPO}_4$. On the other hand, the higher selectivity toward MA showed by the catalyst featured by an excess of phosphorus was related to the higher and nonreversible superficial density of the selective $\delta\text{-VOPO}_4$ as well as to the presence of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

Scheme 3. Synthesis of TMHQ and (all-*rac*)- α -Tocopherol

that dehydrates, under reaction condition, to δ -VOPO₄.^{81,82}

- The fourth and the fifth generations were again the result of VPO precursor synthesis modification. In particular, the addition of Nb as the promoter was shown to be the milestone to further improve ALMA catalyst performance. The effect of Nb, as promoter, was investigated by means of reactivity experiments as well as *in situ* Raman spectroscopy, revealing that the key role of Nb was to enhance and improve the formation of the selective δ -VOPO₄ specie on the surface of VPO by promoting the oxidation of V⁴⁺ into V⁵⁺ under reaction conditions and preventing, at the same time, the over-reduction of V⁴⁺ to V³⁺. Furthermore, it was demonstrated that the positive effect shown by Nb was realized with a very low amount of it, i.e., for a V/Nb atomic ratio as high as 150 while, concentrations higher than the optimal led to a detrimental effect on the catalytic performance due to the generation of an undesired excess quantity of unselective VOPO₄ species such as α I-VOPO₄ and α II-VOPO₄.⁸³

The successful collaboration between Prof. Cavani and Polynt S.p.A. has been recognized by the Scientific Community with the “Medaglia Mario Giacomo Levi” awarded by the Italian Chemical Society in 2017 for the “*Scientific and Technological Development, Scale-up and Industrialization of the Innovations on Maleic Anhydride Production*”.

3. THE UPGRADING OF ALCOHOLS TO CHEMICALS

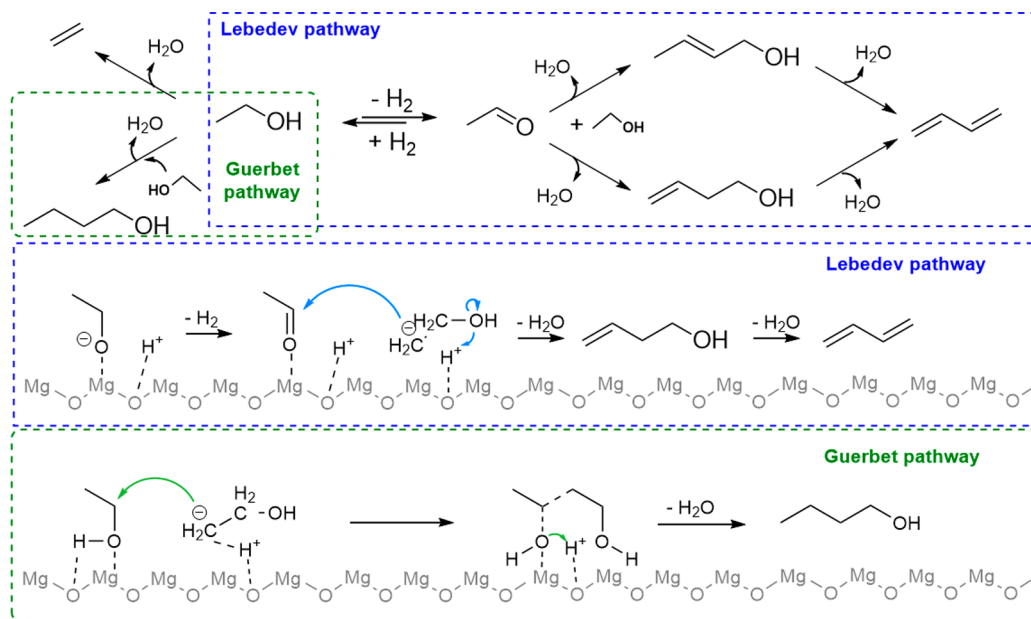
Bioalcohols are emerging as promising platform molecules for the chemical industry due to their increased availability and decreasing costs for the production of a wide plethora of value-added chemicals and fuels. For these reasons, it is not surprising that Cavani was strongly involved in the investigation of innovative catalytic processes aimed to their valorisation. In particular, his interest was focused on methanol, ethanol and glycerol valorisation, with some works related to the direct valorisation, often through selective oxidation processes, of 1-butanol,⁸⁴ 1-decenols,⁸⁵ 1,2-propanediol,⁸⁶ 1,6-hexanediol,⁸⁷ among others. In the following sections, the main valorization strategies of C1 (methanol), C2

(ethanol), and C3 (glycerol) alcohols/polyols, promoted by Cavani's work, are reported.

3.1. The Gas-Phase Methylation of Phenol with Methanol. This work was developed in strong collaboration with the company DSM. Indeed, DSM is interested in the synthesis of methylated phenols that are precursors in the synthesis of 2,3,5-trimethyl-hydroquinone (TMHQ), a key building block in the synthesis of (all-*rac*)- α -tocopherol, which is the most important compound in the vitamin E group (Scheme 3). Cavani is a well-known expert in the field of alkylation of aromatic compounds, being one of the first researchers to fully understand the role of the *in situ* formed formaldehyde in phenol methylation processes.^{88–109} Since the development of an environmentally more friendly and cheaper process toward TMHQ was of industrial importance, the methylation of phenol was considered an interesting approach that promised to meet company targets of developing more sustainable and efficient processes for products already on the market.

In collaboration with Prof. Cavani and his research group, the gas-phase methylations of phenol, *o*-cresol, and 2,6-dimethylphenol (2,6-xylenol) were studied. A new catalyst based on magnesia and gallium oxide with an excellent performance was found^{110–114}. This catalyst is highly active in the rate-limiting step of dehydrogenation of methanol to formaldehyde. The moderate acidity of the gallium centers allows an intramolecular rearrangement of the undesired byproducts of O-methylated phenols. Omitting the addition of gallium, by applying pure MgO, leads to very low catalyst activity. Adding 10% (molar) gallium improved the conversion of phenol from 5% to greater 95%. Furthermore, the role of water was studied in detail. In the case of tris-methylation of phenol, three equiv of water is formed, and further addition of water did not show significant beneficial effects on the catalyst activity or selectivity. However, when 2,6-xylenol was applied as the starting material, the addition of water led to a decrease in the formation of anisole derivatives. DFT calculations and *in situ* FT-IR showed that in the presence of adsorbed water, the adsorption energies of phenolics are lower compared to the dry catalyst. The aromatic ring tends to bend toward the catalyst's surface. This allows the electrophilic attack in *para*-position.

Scheme 4. “The Cavani’s Mechanism” for Butadiene and 1-Butanol Continuous-Flow, Gas-Phase Production over MgO



Furthermore, the presence of water promotes the hydrolysis of ethers, thus lowering the amounts of anisole-based byproducts.

The collaborations between DSM and the group of Cavani on the gas-phase methylations of phenolic substrates were very fruitful and allowed DSM to develop new routes to TMHQ. The co-operation between academia partners and industry resulted in several patent applications and a publication in the field of methylation reactions for aromatic compounds. Cavani is an inspiring person, and he motivates the team members to achieve the project targets. Additionally, his deep understanding of heterogeneous catalysis helps to get an understanding of the reaction mechanism and to find a suitable catalytic system. The co-operation between DSM and Cavani and his co-workers was fruitful, and during the projects not only were scientific outstanding results achieved but also a good relationship was established. For all these achievements, Cavani plays an important role, because his personal skills such as being open minded and friendly, his interest in science, and motivation are outstanding. For all these reasons, the collaboration aimed at the development of innovative catalytic processes for the methylation of other (biobased) aromatic substrates is still ongoing.

3.2. Light Alcohols as Clean and Efficient H-Transfer Reactant for Carbonyl Reduction: Methanol and Ethanol. By keeping the attention on the utilization of short alcohols for the development of innovative continuous-flow processes in the gas-phase, Cavani contributed to the development of the catalytic transfer hydrogenation (CTH) processes for the valorization of biobased aldehydes and ketones. Specifically, short alcohols can be used as reducing agents (i.e., H-donors), avoiding any needs of both high-pressure molecular hydrogen and expensive noble metal catalysts. Interestingly, methanol was used not only for the production of methyl methacrylate and methyl isobutyrate via a complex cascade sequence of methylation, dehydration and H-transfer reactions¹¹⁵ but also as a reducing agent of furfural, this way obtaining not only the corresponding alcohol but also the methyl (and dimethyl) furan, the latter being considered as alternative biobased fuel additives. This approach has been

investigated over both redox (FeVO₄),¹¹⁶ basic (MgO, CaO)^{117,118} or polyfunctional catalysts (Mg/Fe/O)¹¹⁹ and finally compared to the results obtainable in more traditional liquid phase processes in batch systems.¹²⁰ Similarly, also ethanol can be used as an effective H-donor for biomass derived compounds. In this context, Cavani's group was the first to propose performing the CTH of alkyl levulinates with ethanol under continuous-flow and gas-phase conditions. In particular, over a simple and cheap heterogeneous catalyst based on tetragonal ZrO₂, it was possible to achieve complete methyl levulinate conversion and roughly 70% of γ -valerolactone (GVL) yield at 250 °C with a contact time of only 1 s. The deactivation phenomena were investigated in detail, and the superior performance of the gas-phase approach compared to the more traditional batch reactor in liquid phase was demonstrated.^{121,122}

3.3. Bioethanol Upgrading Strategies. Following his inspiring talent in recovering highly promising reactions from the past to be applied in building the future, Cavani has been performing for years as a pioneer of green transition. As from his own words from a perspective: “Ethanol is a suitable, largely available and low-cost biobased starting material for the industrial production of several value-added compounds”,¹²³ his talent in perceiving new concepts in old reactions was devoted to the exploration of bioethanol valorisation via the Lebedev (for the production of biobutadiene, a key bio platform for the synthesis of biobased rubbers) and the Guerbet reactions (for the production of higher alcohols for second-generation biofuel or lubricants).

In particular, Prof. Cavani proposed a revision of the mechanism, also known as “the Cavani’s mechanism” of these two transformations catalyzed by basic oxides (e.g., MgO as a model basic catalyst) in the gas phase with a multifunctional approach (reactivity tests, *in situ* diffuse reflectance infrared Fourier transform spectroscopy - DRIFT, MS analysis, and theoretical modeling) providing a rational description of the key intermediates also shared by the two reaction pathways as well as an innovative concept on the catalyst requirements to the reaction pathway toward 1-butanol (Guerbet reaction) or

butadiene (Lebedev process) summarized in Scheme 4.¹²⁴ Crotyl alcohol and 3-buten-1-ol are precursors for butadiene formation and are the key intermediates of the Lebedev process. On the other hand, the reaction between ethanol and the carbanion in its activated form is likely to explain the formation of the Guerbet alcohol as a primary product (kinetic).

The fascination for the Lebedev reaction was further fed during Cavani's career, exploring physical and reactivity features of MgO based catalysts such as magnesium silicates and Ga-doped derivatives.

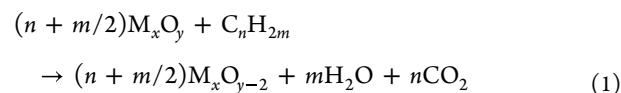
Exploiting the sol-gel technique in order to tune the Mg/Si atomic ratio in MgO/SiO₂ catalysts, found best for butadiene yield and selectivity between 9 and 15, useful combination of strong basic sites for ethanol activation (i.e., the electrons rich surficial oxygens linked to Mg²⁺) and medium-strength Lewis acid sites (associated with Mg²⁺ cations in the proximity of Si⁴⁺) in enhancing the dehydration of alkenols into butadiene have been defined.¹²⁵ The effect of the integration of Ga³⁺ as a promoter in the structure of magnesium silicate on the one-pot conversion of ethanol to butadiene was also explored in order to further correlate the acid/base and dehydrogenative properties of the catalyst with its performances. In particular, the authors found out that the impregnation of a 5% of Ga³⁺ creates new Ga-O(H)-Si sites which are not only able to promote ethanol adsorption and dehydrogenation to acetaldehyde but also foster consecutive condensation reaction to intermediate crotyl alcohol and dehydration toward butadiene.¹²⁶

With an eye to the liquid phase, Cavani, in collaboration with Mazzoni's group, gave an important contribution to the implementation of a new way of thinking the homogeneous side of the Guerbet reaction, not only in order to add new mechanistic insights but with the noble aim to break the boundaries between heterogeneous and homogeneous research approaches to the alcohol homologation. Bioethanol refining is conceived to develop new strategies for production of second-generation biofuels. And the Guerbet reaction is an attractive route for the catalytic upgrading of ethanol to linear and branched higher alcohols, which possess greater energy density and miscibility with conventional fuel compared to their lighter analogue. While simple in principle, this is difficult in application due to several concerns encountered in selectivity and conversion. These drawbacks can be partially avoided by exploiting homogeneous catalysis.¹²⁷ Among the others innovation introduced by Cavani in the field, we can enumerate the implementation of a rigorous carbon balance and the introduction of LCA and engineering assessments applied for the first time to a Guerbet homogeneous catalytic system.¹²⁸ The first phosphine free ruthenium bifunctional complex, competitive in conversion and selectivity with the state of the art, was then employed in a triad catalytic system together with benzoquinone and a base as cocatalysts. The synergistic work of the ruthenium complex for hydrogenation and dehydrogenation, a base that catalyze aldol condensation, and benzoquinone (BQ) as a cocatalyst which favor the selectivity on higher alcohols reducing side reactions lead to unprecedented catalytic activity (up to 88%) and selectivity (up to 97% in C4-C10 alcohols) under mild conditions ($T = 150\text{ }^{\circ}\text{C}$, $t = 4\text{ h}$, $[\text{Ru}] = 0.2\text{ mol } \%$, $\text{BQ} = 1.5\text{ mol } \%$, $\text{NaOEt} = 20\text{ mol } \%$). The catalytic system is also water tolerant, and its reactivity can be extended to bioethanol from waste (e.g., a real matrix from head and tail waste from alcohol distillation

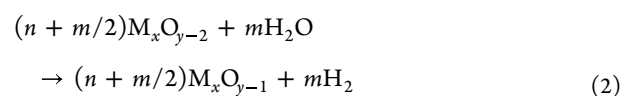
furnished by CAVIRO s.p.a.) toward the production of second-generation biofuels.¹²⁹ The process was patented.¹³⁰

Lately, an innovative catalytic upgrading strategy of biobased alcohols for sustainable aviation fuels production was developed by Cavani's group. In this strategy, a multifunctional catalyst based on Cu finely dispersed over ZrO₂ was proved to be active in promoting a cascade sequence of reactions including: (i) alcohol dehydrogenation to aldehyde, (ii) dehydrogenative coupling to esters, (iii) aldol condensations, (iv) esters and acids ketonization, and (v) catalytic hydrogen transfer; this way allowing the upgrading of ethanol toward C6-C14 linear and branched ketones and alcohols. The results obtained allowed to fill a patent and the scale-up feasibility to pilot plant is currently under investigation by industrial partners.¹³¹

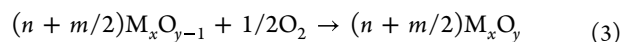
3.4. Mixed-Oxide Catalysts with Spinel Structure for the Valorization of Biomass: The Chemical-Loop Reforming of Bioethanol. Over the past decade, Cavani's work has encompassed processes based on oxidation-reduction reactions, developed for the production of hydrogen, which is emerging as the transportable fuel of the future¹³²⁻¹⁴¹. Very early on, he became interested in chemical loop reforming (CLR) which makes it possible to produce H₂ from different chemical sources by favoring renewable sources such as methanol or ethanol that are likely to be accessible in large quantities. The profitability of a CLR process requires low separation costs; this can be achieved by carrying out the process in two or three alternating steps, allowing H₂ to be separated from the carbon oxides formed (Figure 7a). The first step produces a valuable H₂/CO_x steam from reductants such as light alcohols or oxygen-carrying materials (M_xO_y):



After the first step, the reduced oxygen carrier material is transferred to a second reactor, where it is oxidized by steam to produce hydrogen:



The first step mainly leads to a mixture of CO_x and H₂ and also almost systematically to the formation of carbon on the surface of the carrier which generates CO_x during the second reoxidation step preventing the obtention of high pure H₂ during this step. The formation of carbide from oxygen-carrying materials is also observed and leads to the same drawback. The material often cannot be completely reoxidized by water and that is why a third step such as reoxidation by air is considered:¹⁴²



Cavani and co-workers studied such a process with the aim of making it functional by choosing very early on an oxygen carrier based on metal oxides and, more specifically, binary or ternary spinel mixed oxides containing iron. Spinel oxides based on iron with the formula AFe₂O₄ where A is a transition metal such as Co, Ni, Cu or Mn which have a redox couple allowing, like iron, the materials to be efficient as an oxygen and electron carrier. The thermal stability and the redox properties of these ferrites had previously led the team to use

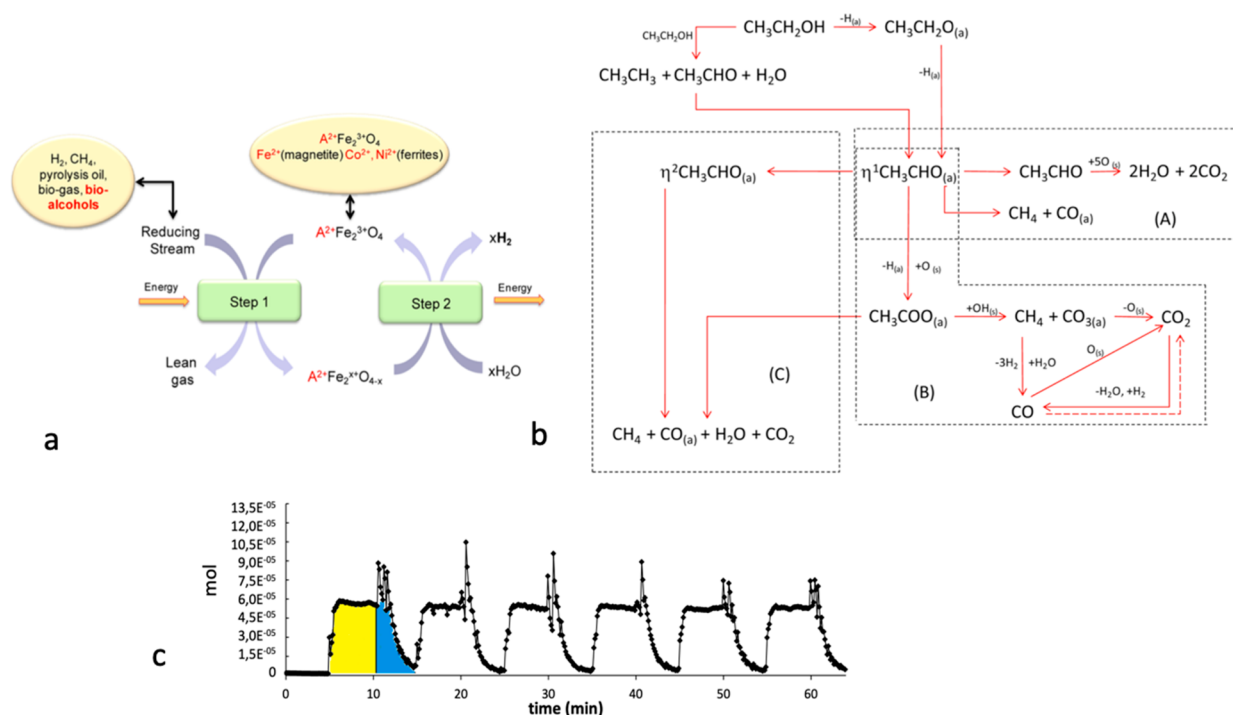


Figure 5. a) Process of chemical looping for the production of H_2 from renewable sources. Reproduced from ref 134. Copyright 2013 America Chemical Society. b) Reaction scheme of ethanol adsorption and transformation Co-ferrite (A), Ni-ferrite (B) and magnetite (C) c) Evolution of H_2 mass spectroscopy signal as a function of time in the cycling process over magnetite. Reproduced with permission from ref 138. Copyright 2015 Royal Society of Chemistry.

them as catalysts in the methylation of phenol.¹⁴³ Other important properties such as their heat capacity, their resistance to attrition and to coke formation and accumulation, their low cost and low toxicity make them oxygen carriers of choice.¹⁴² If the first more fundamental studies focused only on magnetite Fe_3O_4 and CoFe_2O_4 , they then concerned all of the ferrites. The objectives of the different studies were consistent and geared to (i) gain fundamental knowledge on the CLR process, (ii) improve the activity and stability with high conversion rates in cycling steps, (iii) minimize carbon deposition or carbide formation while maintaining full cyclability. Fundamental studies allowed determination of the pathways for anaerobic oxidation of ethanol followed over different ferrites (Figure 5b). These pathways all started with the dehydrogenation to acetaldehyde which was either oxidized to acetates on Ni-ferrite, decomposed to CO and methane on Co-ferrite or completely oxidized on magnetite.¹³⁴ This showed that the nature of the ferrite was important for both the first and second steps of cycling. Following the hydrogen mass spectroscopy signal also allowed to study the repeatability of the cycling (Figure 5c). The first part of the repeated signal (in yellow) represented the trend of H_2 production from ethanol in the first step, while the second part twice less intense (in blue) represented that obtained from water.¹³⁸ The studies of the materials showed that ferrites with Co, Ni, Cu and Mn, lead to higher reduction extents than magnetite, leading to more effective carrier materials. However, they also lead to the formation of more carbides and coke that is not totally removed by H_2O . The later can nevertheless be minimized by using short-time-cycle steps. Co-ferrite is very effective in cycling but accumulates a large amount of coke. Ideally, coke should be unreactive during the reoxidation, in order to avoid being transformed into CO and CO_2 and could

be removed by periodically adding a third step to burn this coke left over by air; in this sense, the best material would be Ni-ferrite, whereas Co or Cu-ferrites, which form Fe carbide that can hardly be reoxidized during the treatment with steam, would be less advantageous. Concerning Cu spinel, a part of Cu segregates in the form of metallic Cu, which did not enter the spinel structure upon reoxidation with steam. Substitution of Cu by Mn hindered carbon deposition, but slow down the reduction by ethanol, which is mainly dehydrogenated.^{139,141} These last studies clearly show that productivity and selectivity are opposite requirements in the development of an oxygen carrier material for the chemical-loop production of H_2 from ethanol. Either insufficiency in reactivity, stability and recyclability; physical strength and attrition resistance; tendency to form and accumulate coke; or oxygen-carrying capacity are observed. These pioneering studies published over the years were instrumental to further studies using more complex mixed oxides as oxygen carriers and to design more efficient reactors for solid circulation. In the coming years, the CLR technology will remain an active research area for an economically viable production of hydrogen utilizing renewable feedstock like bioalcohols, and Fabrizio's work significantly contributed to our current understanding of the limiting steps of the process.

Adding some comments on Fabrizio as a person behind science, I can say that, in a scientific world where competition often takes center stage, he has consistently valued friendship over other things. He has managed to stay down-to-earth, even in the face of remarkable success. Moreover, he has been instrumental in shaping successive generations of students, passing on his passion for science, and motivating them to express their talent and creativity in the lab and in the scientific community. I can honestly say I have yet to come across a

student who does not hold him in high regard. Fabrizio's ability to strike that balance between achievement and humility sets him apart as a true inspiration. His legacy of nurturing talent and fostering genuine camaraderie will leave all of us who have had the privilege to know him with unforgettable memories and will leave a lasting mark.

3.5. On the Selective Transformation of Glycerol to Acrolein/Acrylic Acid. As became clear a few years ago, the challenge of creating a sustainable future involves addressing changes in the chemical industry, with a transition toward a more sustainable chemistry, in which a reconceptualization of the industry and its products must be given, and in which both the use of renewable raw materials and the management of production waste must play a fundamental role in order to better protect the environment.¹⁴⁴ In this context, studies on the selective transformation of alcohols and, more specifically, of polyalcohols such as glycerol and derivatives, using acid and/or redox catalysts, have meant an important advance in the possible substitution of some of the current processes derived from petroleum.¹⁴⁵ Studies on the selective transformation in the gas phase of glycerol and other polyalcohols have focused not only on the synthesis and optimization of effective catalytic systems but also on the study of the nature of the active centers and reaction schemes, trying to find out all byproducts formed by parallel and consecutive reactions (also those products formed by homogeneous reactions) and the influence of reaction conditions on the formation of reaction products.

Cavani et al.^{146,147} initially studied the synthesis of acrolein by dehydration of glycerol, in the gas phase, catalyzed by sulfated zirconia catalysts, since the acid properties, but also redox, of these materials were well-known. This study focused on finding out the reaction conditions in which both heterogeneous catalysis processes occurred, as well as the undesired ones of homogeneous catalysis, as well as the role that oxygen cofeeding could play (both in the selectivity and in the catalyst deactivation). The best selectivity to acrolein (42%) obtained with a glycerol conversion of 49% for a sulfated zirconia catalyst was achieved by combining conditions that limited the appearance of consecutive reactions (with the formation of acetaldehyde and heavy compounds from acrolein) and minimizing the mass transfer limitations between catalyst particles. In addition, they observed that the formation of acrolein occurs only in the presence of Brønsted acid sites, while the appearance of a homogeneous reaction and/or the presence of Lewis acid sites (using for example ZrO_2) led to the formation of similar byproducts, although the glycerol conversion was always higher in the presence of ZrO_2 catalyst.

On the other hand, and working on sulfated zirconia catalysts,¹⁴⁷ they observed that (i) the sulfate content in the catalyst affects not only the glycerol conversion but also the catalyst decay (very low for catalysts with sulfate content of ca. 2.0 wt % SO_4 , and higher for catalysts with sulfate contents higher than 4.0 wt % SO_4); (ii) there are several (reversible) phenomena that affect the deactivation of the catalyst, such as the reduction of the sulfate groups (to sulfite) of the catalyst or the accumulation of organic residues (precursors of coke formation); (iii) an irreversible deactivation is also observed, as a consequence of a loss of S from the catalyst (due to the hydrolysis of sulfate groups and the formation of volatile esters), more important in catalysts with higher sulfur contents. Accordingly, they proposed some partial solution for the

elimination of the deactivation of these catalysts.¹⁴⁷ Thus, the loss of catalytic activity due to the reduction of the catalyst can be recovered with an oxygen treatment of the catalyst, which favors the reoxidation of the sulfite groups to sulfate. With respect to the formation of heavy compounds, it became less formation of heavy compounds when the reaction was carried out in the presence of oxygen (with the formation of carbon oxides), which also favor a lower catalyst decay.

These results have been of special interest to better understand those reactions (parallel and consecutive) that occur during the gas phase dehydration of glycerol to acrolein, with a clear difference between the reaction conditions that favor homogeneous catalysis processes and those in those that favor heterogeneous catalysis. And, we also know those products that are formed in the presence of catalysts with Lewis acid sites (such as ketals and heavy compounds) of those that are produced in the presence of Brønsted acid sites (as acrolein). In addition, they have also pointed out key aspects for the possible use of catalysts based on sulfated zirconia in reactions catalyzed by acid sites at high temperatures.

On the other hand, metal oxide bronzes are a versatile family of materials with wide functional properties and applicabilities. They are usually defined as partially reduced transition metal oxide phases, with the general formula $\text{A}_x\text{M}\text{O}_n$, where A is a cation (i.e., Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , etc.) and M is a transition element (generally W, but also Mo, V, Nb, Ta or Ti, or mixtures of these elements, with different average oxidation states).¹⁴⁸ Therefore, they could present elements with different oxidation states, depending on the composition and/or method of preparation-activation, which could be stabilized by incorporating electropositive cations. Consequently, their ability to admit a wide variety of elements within their crystal lattice offers an interesting possibility to create multifunctional materials (with the possible presence of acid or redox sites).

Among them, hexagonal tungsten oxide bronzes, HTBs also named as $h\text{-WO}_3$, with a general formula of $\text{A}_x\text{W}_{1-x}^{6+}\text{W}_x^{5+}\text{O}_z$, with the cation A compensating the charge deficiency as a consequence of the presence of some W^{5+} cations, are one of the most studied systems.¹⁴⁸ Their crystalline structure is made up of corner-sharing WO_6 octahedra that position themselves in the three-dimensional space to form three-sided and six-sided channels that give rise to tunnels running along the c direction.

In a first approach, it was observed that NH_4^+ -containing $h\text{-WO}_3$ catalysts, synthesized hydrothermally, could be transformed into an acid catalyst after being heat-treated in N_2 at ca. 400 °C, with an acid strength (and density of acid sites) higher than that observed in the corresponding stoichiometric monoclinic tungsten oxide ($m\text{-WO}_3$).¹⁴⁹ In addition, these activated $h\text{-WO}_3$ catalysts showed high activity and relatively high selectivity during the transformation of glycerol to acrolein. The acid characteristics of this material, was related to the presence of Brønsted acid sites, formed during the partial elimination of ammonium cations in the activation step in an inert atmosphere. But, unfortunately, the thermal stability of $h\text{-WO}_3$ was relatively low, especially during the catalytic tests in the presence of oxygen in the feed, as a consequence of the removal of remaining ammonium cations (which apparently stabilized the HTB structure) and the final presence of $m\text{-WO}_3$ in spent. However, the thermal stability of HTBs was improved when W atoms were partially substituted by other transition elements.¹⁴⁹ In fact, these promoted catalysts

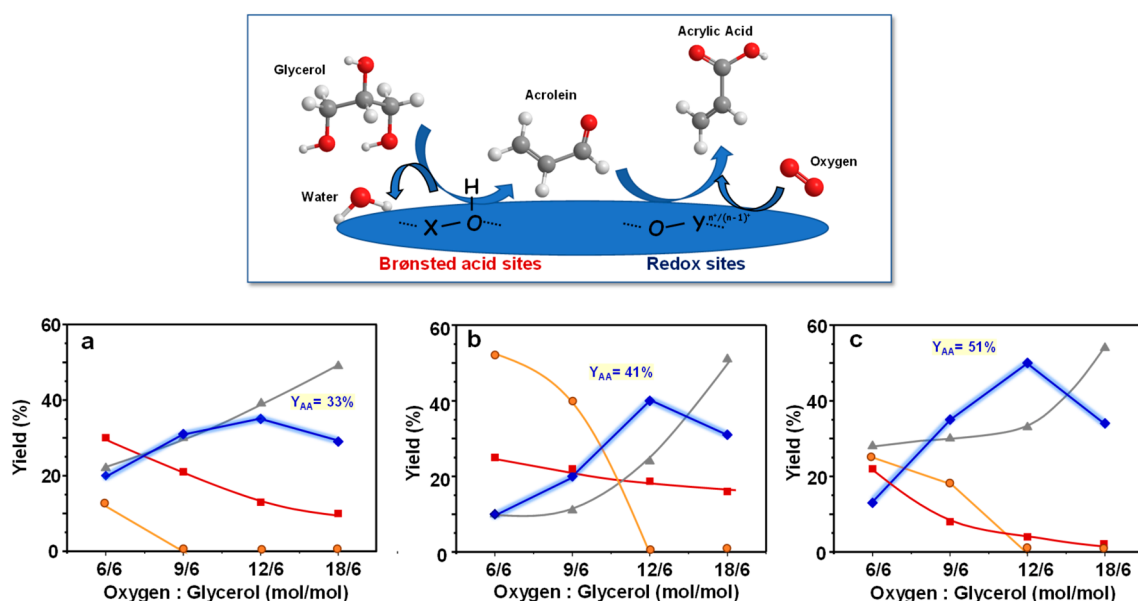


Figure 6. Main reaction products for acrolein oxidation of $h\text{-W}_{0.76}\text{V}_{0.33}\text{O}_z$ (a), $h\text{-W}_{0.74}\text{Nb}_{0.13}\text{V}_{0.13}\text{O}_z$ (b), and $\text{W}_{0.67}\text{Mo}_{0.30}\text{V}_{0.03}\text{O}_z$ (c) as a function of the molar ratio of the oxygen/glycerol. Symbols: selectivity to acrylic acid (blue \blacklozenge), acrolein (red \blacksquare), heavy compounds (orange \bullet), and CO_x (gray \blacktriangle). Glycerol conversion was always complete in all cases. After refs 150,152. Glycerol and water molar ratio constants were 6 and 40%, respectively.

were stable during the activation step, in an inert atmosphere, up to 500 °C (in the case of Ti-containing $h\text{-WO}_3$, named as $h\text{-WTiO}_x$)¹⁵⁰ or 600 °C (in the case of V-, Nb, Mo-containing $h\text{-WO}_3$; named as $h\text{-WMO}_x$),^{149,151–153} favoring also a high stability during the catalytic tests of glycerol oxidehydration (in the presence of oxygen) at reaction temperatures up to 400 °C. In addition, the incorporation of these transition metal in $h\text{-WMO}_x$ promoted also important modifications of the catalytic performance of $h\text{-WO}_3$. The preservation of the hexagonal phase in metal-promoted HTB ($h\text{-W}_{1-x}\text{M}_x\text{O}_z$), was also unambiguously determined by HR-TEM/SAED. When vanadium was incorporated into the $h\text{-WO}_3$ framework (i.e., $h\text{-W}_{1-x}\text{V}_x\text{O}_z$, with $x < 0.30$) it was observed a small decrease in the number of acid sites (related to W ions) but the appearance of redox properties (related to V species).¹⁴⁹ Thus, yield of acrylic acid of ca. 25% (with yield of acrolein and carbon oxides of 11 and 47%, respectively) was observed during the one-pot selective aerobic transformation of glycerol.¹⁴⁹ The reaction in this case occurs by the presence of two different functions: (i) the acid sites, related to W-sites, which catalyze the selective transformation of glycerol to acrolein; and, (ii) the redox sites, related to V-sites, which are active and selective in the partial oxidation of acrolein to acrylic acid. In addition, not only the density and strength of acid sites, but also the concentration of V-sites and the average oxidation state of vanadium ($\text{V}^{4+}/\text{V}^{5+}$ ratio) appeared also as a key element for the oxidation reaction.¹⁴⁹ In this way, it was also observed that the $\text{V}^{4+}/\text{V}^{5+}$ ratio could be also optimized by tailoring the glycerol/oxygen ratio in the feed. Subsequently, and after the optimization of the reaction conditions, a yield of acrylic acid of ca. 30% (with a remanent yield of acrolein of ca. 12%) was confirmed when working at higher oxygen/glycerol ratios in the field (Figure 6).

In a different trend, the isomorphous incorporation of element with low and stable oxidation state as Ti^{4+} , but specially Nb^{5+} (i.e., $h\text{-W}_{1-x}\text{Ti}_x\text{O}_z$ ¹⁵² and $h\text{-W}_{1-x}\text{Nb}_x\text{O}_z$, with $x < 0.30$),¹⁵⁰ modify only the acid characteristics with respect to

pure HTB, with a higher thermal stability during the catalyst activation, but also after the catalytic tests in the aerobic transformation of glycerol. However, as these materials only present acid characteristics, they showed an acrolein yield of ca. 73.0 and 76.0%, respectively, higher than that observed over pure $h\text{-WO}_3$ (with an acrolein yield of ca. 67.0%). We must note that the presence of oxygen is not formally required during glycerol dehydration, but the presence of oxygen prevents a fast catalyst deactivation allowing the oxidation of carbon deposit during the catalytic test.^{150,152}

In a later stage, the development of multifunctional catalysts was also studied, optimizing both the acid and the redox characteristics of catalysts in order to improve the catalytic properties in the one-step process from glycerol to acrylic acid. In this way, the synthesis of V- and Nb-containing HTB materials, i.e., $h\text{-W}_{1-x}(\text{Nb}/\text{V})_x\text{O}_z$ with $x < 0.30$, was initially proposed, which showed differences in both acid and redox properties with respect to bimetallic materials. Thus, the catalysts $h\text{-W}_{0.74}\text{Nb}_{0.13}\text{V}_{0.13}\text{O}_z$, with Nb^{5+} and $\text{V}^{4+/5+}$ species incorporated in the framework of HTB structure, presented a yield of acrylic acid and acrolein of ca. 33 and 17%, respectively (with a yield of CO_x of 40%) during the glycerol oxidehydration at 290 °C. In addition, when comparing both the catalytic results and the nature of V species on the catalyst surface of $h\text{-W}_{0.76}\text{V}_{0.33}\text{O}_z$ and $h\text{-W}_{0.74}\text{Nb}_{0.13}\text{V}_{0.13}\text{O}_z$, it was proposed that the better stability and yield of acrylic acid Nb,V-containing catalyst, could be related to a higher stabilization of V^{4+} species in the bronze, which seems to be promoted by the presence of Nb^{5+} .

Another strategy has been the development of catalysts based on V-containing W–Mo-oxide bronzes (i.e., $\text{W}_{1-x}(\text{Mo}/\text{V})_x\text{O}_z$). In this case, the HTB structure was observed for samples with Mo/W ratio lower 0.30, whereas a pseudocrystalline phase was observed for samples with Mo/W ratio higher than 0.40. In addition, the atomic ratio of the elements was a key aspect in order to tune acid and redox properties, but also resulted to be also a key factor in the size of the crystals and

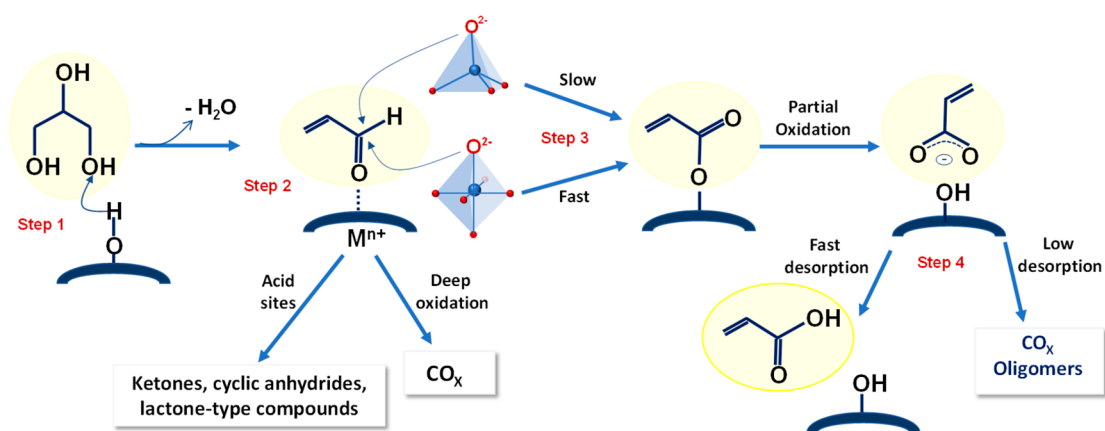


Figure 7. Reaction mechanism for the oxidative hydrogenation of glycerol to acrolein and acrylic acid on catalysts presenting both acid sites and redox sites (vanadium is the active redox element). Adapted with permission from ref 154. Copyright 2017 European Chemical Societies Publishing.

their log-range distribution. From all the catalysts studied, the better catalytic performance was observed for a catalyst, with formula $W_{0.67}Mo_{0.30}V_{0.03}O_z$, presenting on pseudocrystalline phase (with lattice planes equally spaced at about 3.8 Å).

In the best reaction conditions, it was observed that the yield to acrylic acid, at an oxygen/glycerol molar ratio of 2 (i.e., partial pressure of oxygen and glycerol of 12 and 6, respectively), increases in the order (Figure 6): $h-W_{0.76}V_{0.33}O_z$ ($Y = 33\%$) < $h-W_{0.74}Nb_{0.13}V_{0.13}O_z$ (41%) < $W_{0.67}Mo_{0.30}V_{0.03}O_z$ ($Y = 51\%$); being the tricomponent W-Mo-V-O one of the catalysts with the highest yield to acrylic acid of those reported in the literature for the one-pot synthesis of acrylic acid from glycerol by using a single multifunctional catalyst.^{151,153}

However, at an oxygen/glycerol molar ratio of 1 (i.e., partial pressure of oxygen and glycerol of 6 and 6, respectively), the opposite trend has been observed, with the sample $W_{0.67}Mo_{0.30}V_{0.03}O_z$ presenting the higher formation of heavy compounds and the lower selectivity to acrylic acid. These results suggest that one of the most important parameters affecting the catalytic behavior is the partial pressure of oxygen. In this way, it has been proposed that a high oxygen partial pressure enhanced the reoxidation process of the catalyst (the rate-determining step in the redox mechanism of acrolein transformation into acrylic acid is the oxidation of the reduced V sites into V^{5+}) and boosted the selectivity to acrylic acid (the surface concentration of the oxidizing species is thus affected by oxygen partial pressure).¹⁵¹ Thus, the different behavior of catalysts strongly depends on both their composition and their redox properties.¹⁵³

According to these results, it is clear that the design of suitable catalysts for the direct transformation of glycerol into acrylic acid, considering one-pot conversion, is very complex, because it is necessary to tune both acid and redox sites properties. In this way, it has been also working on fundamental studies in order to understand possible structure–reactivity correlations of catalysts. In this way, a comparison between the physicochemical and the catalytic properties of catalysts presenting both acid sites and/or redox sites (the last only related to different V-species) was also proposed. It was observed that $h-W_{1-x}V_xO_z$ (with the majority of vanadium, in octahedral coordination, incorporated in the framework of HTB) presented higher selectivity than VCoAPO-5 (with the majority of vanadium sites, in tetrahedral coordination, incorporated in the framework of AlPO-5

structure) or vanadyl pyrophosphate ($VO_2P_2O_7$, with vanadium pairs of VO_6 octahedra joined by the edges). In addition, the catalytic activity of V-sites in $h-W_{1-x}V_xO_z$ was higher than those in VCoAPO-5 or $VO_2P_2O_7$. Accordingly, a reaction mechanism for the oxidative hydrogenation of glycerol on acid catalysts with vanadium as the active redox element has been also proposed, in which we can conclude several key aspects (Figure 7): (i) Glycerol is selectively transformed into acrolein on Brønsted acid sites (step 1); (ii) A rapid desorption of acrolein is required in order to avoid consecutive reactions (step 2); (iii) Isolated octahedral V-sites favor a rapid oxidative activation of acrolein forming a carbonyl-bonded acrolein (step 3); (iv) The presence of acid sites could also control the desorption of reaction products (step 4); (v) The presence of V^{5+} sites favors the formation of CO_x avoiding the formation of heavy compounds; (vi) Accordingly, both V^{4+} and V^{5+} sites are required but presenting relatively high V^{4+}/V^{5+} ratios.

We must indicate that the formation of ketones, cyclic anhydrides and lactone-type compounds have been described as a consequence of the presence of Lewis acid sites in some of the last catalysts^{151,154} (Figure 7). This is the case of the formation of other byproducts such as cyclic ethers (1,3-dioxan-5-ol or 1,3-dioxolan-4-yl-methanol, formed by the reaction between glycerol and formaldehyde or acetaldehyde) confirmed by means of ESI-MS.

More recently it has been also studied the oxidative hydrogenation of 1,2-propanediol to propanoic acid with bifunctional catalysts, some of them similar to those studied for glycerol transformation, since could be similar reaction.⁸⁶ However, the results achieved for both reactions show strong differences, with the transformation of 1,2-propanediol presenting lower selectivity to the corresponding carboxylic compound (ca. 13% yield of propionic acid over a W–V–Mo mixed oxide catalyst). On the other hand, and from the study on the intermediate species involved in this reaction by means of IR spectroscopy, it has been concluded that the oxidative cleavage reaction rather than the oxidative hydrogenation is favored during the transformation of 1,2-propanediol, being C1–C2 compounds, in addition to acetals, the main reaction products. Similar behaviors were also observed starting from 1,2-cyclohexanediol.¹⁵⁵

4. VALORIZATION OF BIOMASS AND CO₂ DERIVATIVES

More recently, great efforts have been devoted to the valorization of biobased platform chemicals and in the valorization of CO₂ following different strategies. Cavani's contribution on these topics would be worth an entire review alone. However, we decided to select and focus the following lines only on two different compounds (or families of compounds), namely, 5-hydroxymethyl furfural (HMF) and organic carbonates.

HMF is a key biobased platform for the production of renewable intermediates, monomers, and biofuels. Its production from lignocellulosic biomass follows a cascade sequence of acid-catalyzed reactions and still suffers of poor economic and environmental sustainability. In this context, Cavani contributed to the development of an alternative synthesis from fructose and inulin in aqueous media, in the presence of catalytic amount of a heterogeneous, recyclable, niobium and/or zirconium phosphate under microwave heating (HMF yield of about 40% in 8 min of reaction time).¹⁵⁶ Among the HMF valorization strategy, huge efforts have been devoted to the development of innovative catalytic systems able to promote the selective HMF oxidation toward furandicarboxylic acid (FDCA) in the presence of molecular oxygen. Cavani and Albonetti have in depth investigated several catalytic systems based on either monometallic Au nanoparticles supported over TiO₂, CeO₂,¹⁵⁷ Ce_xZr_{1-x}O₂,^{158,159} Al₂O₃,¹⁶⁰ carbons,¹⁶¹ or bimetallic Cu–Au/TiO₂¹⁶² and Pd–Au¹⁶³ systems. Notably, thanks to the in-depth investigation and understanding of the reaction mechanism, the group has managed to develop an innovative catalytic system based on AuPd–nNiO (n: nanosized) highly active and selective under base-free conditions. The synergy between Au, Pd and Ni was proved to be pivotal allowing to achieve 95% HMF conversion with a FDCA yield equal to 70%.¹⁶⁴

Since 2014, Cavani's group has been active in the development of innovative catalytic processes for the synthesis and use of organic carbonates (OCs) as alternative reagents for alkylation and carbonylation reactions. Organic carbonates (R–O–C(O)O–R) are generally characterized by a very low toxicity, good biodegradability and because of their high boiling point, that lowers the emission of volatile organic compounds in the atmosphere (VOCs), and high solvency, they find wide utilization as aprotic polar solvents.¹⁶⁵ As a matter of fact, organic carbonates are considered suitable products for the valorization of CO₂ due to their highly oxidized and low-energy content. In this regard, Cavani and Tabanelli have investigated in depth the possibility to use organic carbonates as alternative alkylating agents for phenolics, avoiding the needs of toxic epoxides or alkyl halides. In particular, both ethylene carbonate (EC)¹⁶⁶ and glycerol carbonate (GlyC)¹⁶⁷ were successfully used for the alkylation of phenol in the presence of a basic catalyst, in the liquid phase without the needs for any external solvents; while diethyl carbonate (DEC) was used as effective ethylating agent for the same substrate under continuous-flow and gas phase conditions.¹⁶⁸ Notably, GlyC was also used, for the first time in literature, in the alkylation of catechol, this way discovering a completely innovative way for the synthesis of substituted benzodioxanes.¹⁶⁹ It is worth noting that Cavani's group was also the first to optimize the synthesis of catechol carbonate

(CC) via the carbonate interchange reaction between catechol and dimethyl carbonate. CC is an elusive OC, whose formation suffers of unfavored equilibrium limitation; therefore, it has scarcely been investigated in the literature. Interestingly, CC isolated yields were successfully increased from 10 to 95% thanks to the implementation of an innovative reactive distillation systems based on the selective adsorption of the coproduced methanol inside 4 Å molecular sieves.¹⁷⁰ Once unlocked the availability of low cost CC, its peculiar reactivity as alternative carbonyl source have been foreseen and proved for a series of highly interesting applications like the selective synthesis of symmetric carbonates in super mild conditions¹⁷¹ and the isocyanate-free production of ureas and polyureas in solvent- and catalyst-free conditions.^{172,173}

5. CONCLUDING REMARKS

Fabrizio Cavani is one of the pioneers and world-leading experts in the development of heterogeneous catalysts for sustainable important industrial chemical processes. He has contributed to the development and understanding of heterogeneous catalysts, especially on the synthesis, scale up of mixed oxide catalysts, and fundamental studies that help the direction of understanding better the reaction mechanisms and the role of the developed catalytic systems. One of the most important and favorable topics of Fabrizio was the development of VPO catalysts for the selective oxidation of *n*-butane to maleic anhydride. Other examples include development of heterogeneous catalysts for the valorization of biomass derived molecules, for example, (i) the development of catalytic transfer hydrogenation processes, (ii) the bioethanol valorization via the Lebedev and the Guerbet reactions, and (iii) the selective transformation of glycerol to acrolein and acrylic acid. In 2017, Fabrizio was the recipient of the “Medaglia Mario Giacomo Levi” award by the Italian Chemical Society in 2017 for the “Scientific and Technological Development, Scale-up and Industrialization of the Innovations on Maleic Anhydride Production” recognizing the long and one of the most successful academic-industrial collaborations in Italy with Polynt. Recently, Fabrizio has established with academic colleagues the Center for Chemical Catalysis (C³) at the University of Bologna, focusing on the development of green and sustainable catalytic chemical processes focusing on the expansion of stronger academic-industrial partnerships. We wish Fabrizio well in his successful career and leadership in the near future.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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