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Perspective

Industrial Synthesis of Allyl Alcohols: Outlook and Challenges for a Sustainable Production

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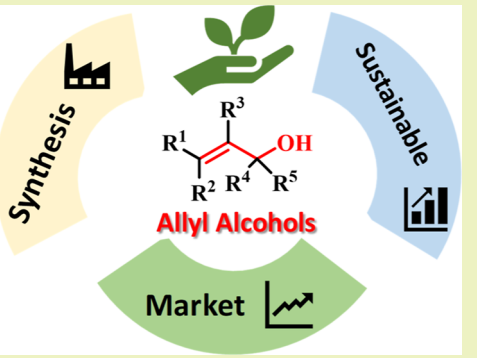
ABSTRACT: Allyl alcohols are essential fine chemicals in modern manufacturing, employed in a plethora of fields from vitamins to fragrances and drugs. In accordance with this, a plethora of academic synthesis with particular methodologies have been published in the last 20 years, however, these synthetic approaches do not always fulfill neither the sustainability nor the industrial expectations, and any update on sustainable industrial synthesis of allyl alcohols and future developments is barely found. Indeed, the environmental and economic costs associated with the synthesis of allyl alcohols are often unaddressed, despite the sustainability of the synthetic process is key for a modern industry. Here, we first summarize the main synthetic procedures for allyl alcohols studied in academic laboratories, most of them catalytic, and then we put into perspective the industrial manufacturing of allyl alcohols and the market involved, with trends and challenges, contextualized within the current, mandatory, modern sustainability principles. The comparison unveils some mismatches between the academic studies and the industrial needs for allyl alcohols, thus we offer here some ideas about future synthetic developments in the context of sustainable chemistry. We hope that this review will present an overview of how allyl alcohols are actually produced and how they should be produced in the near future, remarking the catalysis as a key factor.



KEYWORDS: *allyl alcohol, industrial synthesis, catalysis, palladium, hydrogenation, sustainability*

1. INTRODUCTION

Fine chemicals are a fundamental pillar of industry, and their large−scale production is necessary to meet the needs of the different actors involved (producers, developers, customers).[1] These fine chemicals, as commodities, often require multi−ton productions not only for their distribution but also to manufacture substances of greater complexity. Indeed, fine chemicals already account for a $185 billion market size, expected to exceed $340 billion by the end of 2033, at a compound annual growth rate (CAGR) of 7%.[2] However, the fine chemical industry is generally associated with relatively low profit margins if compared to more specialized sectors, which together with its flexibility to change manufacturing reaction procedures (generally in batch), boost this industry to optimize their synthetic processes quite often and decrease manufacturing costs, especially if these improvements are applied to the limiting factor of the process such as the catalytic reaction.[3]

An example of fine chemicals production is the manufacture of allyl alcohols. This family of compounds are industrial chemical products on their own or widespread intermediates to fabricate fragrances, lubricants, surfactants, defoamers or vitamins, among others.[4] The use of metal-based catalysts is essential for the industrial synthesis of allyl alcohols but, in turn, is the most expensive part of the process.[5] The lower the amount of catalyst in the process, the higher the reduction of costs, ideally up to achieve that the catalyst is no longer a critical factor that entails the associated costs, instead providing economic, environmental and logistical benefits.[6] Therefore, it is not surprising that many catalytic research laboratories worldwide have included the synthesis of allyl alcohols as a preferential topic in their research programs, and Figure 1 shows the exponential growth in publications observed during the last 45 years.

The market size of allyl alcohols corroborates the need of investigating in new synthetic processes. Figure 1 also shows that the global allyl alcohol market expects a relevant growth in the next decade, at a compound annual growth rate (CAGR) of 6% for the period 2024−2034.[7] This striking increase is logical since the demand for allyl alcohols is expected to double in the next 10 years, associated with the constant demand not only of the very same allyl alcohols as final products but also for subsequent products obtained from them. The annual consumption of allyl alcohols as intermediates is already estimated at >1 million tons per year, for the manufacture of vitamins, resins for lenses and

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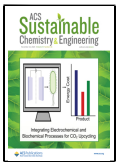

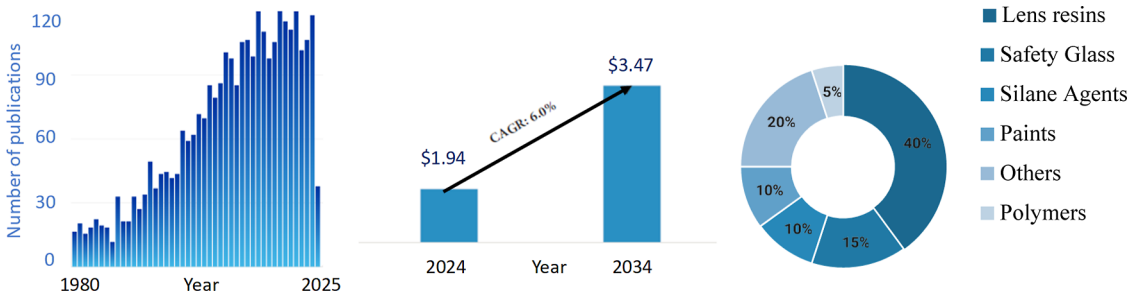

Figure 1. From left to right. Number of academic publications (patents excluded) per year for the term "synthesis of allyl alcohols" according to Scifinder during the period 1980–2025 (2025 is still uncomplete), compound annual growth rate 2026–2033 (CAGR) for allyl alcohols, and main applications divided by industrial sectors.

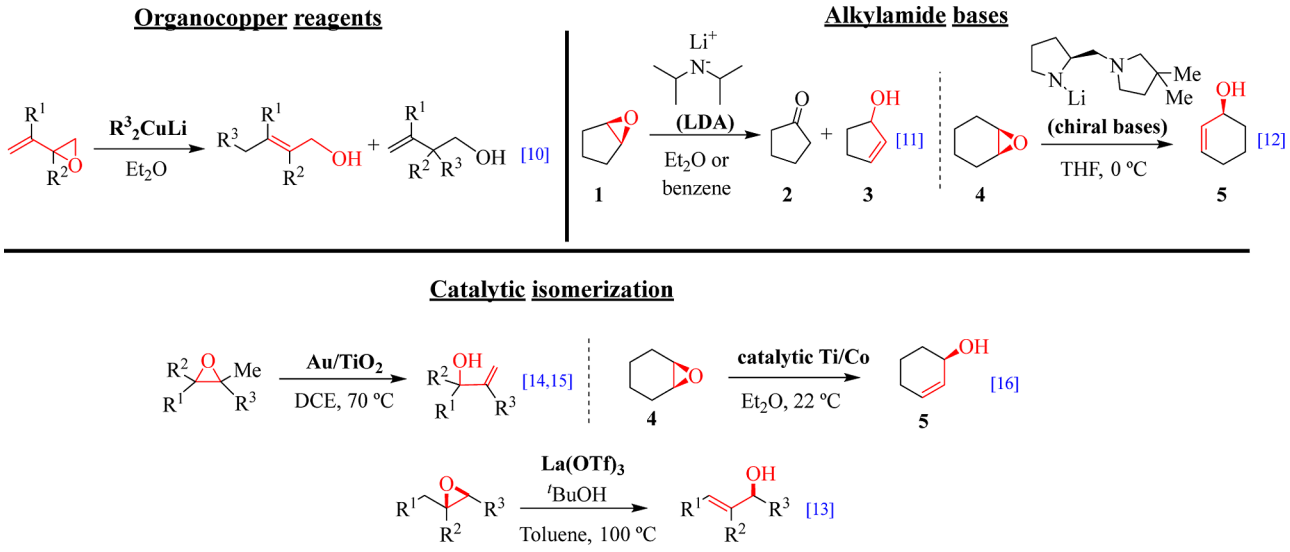

Figure 2. A summary of the synthetic approaches mainly found in different reviews for the synthesis of allyl alcohols (for example **3** and **5**) by a metal–catalyzed isomerization reaction of the corresponding epoxides.[10−16]

glasses, and, as an intermediate agent, in the manufacture of paints, coatings, fragrances, and many other products (see Figure 1). Besides, the allyl alcohol market shows stable values, which can be associated with the fact that some of them (for instance allyl alcohol and methylated derivatives) can be considered as a commodity rather than a fine chemical. For instance, the manufacturing process of allyl alcohols within biorefinery plants is accepted as one of the most potentially profitable reactions,[8] since it also provides materials such as acrolein and acetol, substances manufactured in large quantities for use in bulk. However, on the fine chemical side, allyl alcohols can be intermediates of very specialized products, such as the terpinolene allyl alcohol for the production of the fragrance terpinen−4−ol.[9] Therefore, despite the fact that the market volume of allyl alcohols is not as high as other organic compounds such as raw alkenes or epoxides, any development that seeks to minimize production costs, such as the optimization and recovery of catalysts (one of the most influential factors in the economics of the process) is of great interest to industry. The cost reduction on the catalytic metal, applied to a product that is sold in tons, is much more noticeable.

Here we present an overview of the main synthetic methods studied in the academic laboratories for the synthesis of allyl alcohols during the last years, exemplified by a number of reviews on the respective synthetic methodologies. Then, we analyze the patents appeared during the last 20 years in the field, to correlate both the academic and industrial synthesis, within an overall view of the ally alcohol market, including the value chain. In this way, we detect some of the main companies around the Globe involved in the synthesis, use as intermediates and distribution of allyl alcohols, their possible needs according to the patented technologies, and how academic research can fill any gap in the near future. It must be noticed that the present review does not intend to give an exhaustive enumeration of synthetic methods for allyl alcohols, neither explain them in detail, since this information can be found in the cited reviews and articles, but a comparative outlook of how allyl alcohols are prepared at the academic and industry level, to unveil coincidences and differences, and provide new pathways to be followed, sustainable in nature if possible. Nevertheless, in a middle position between base and fine chemicals, an overview of the production methods and market size for allyl alcohols has been significantly ignored in the literature during the last two decades,[5] hence this Perspective, beyond palliating the lack of recent reviews for alcohol synthesis and proposing solutions on how to substitute petrochemical−by renewable-based processes, provides a holistic view to the Reader about the allyl alcohol production field, from academic to industrial research to the market value chain.

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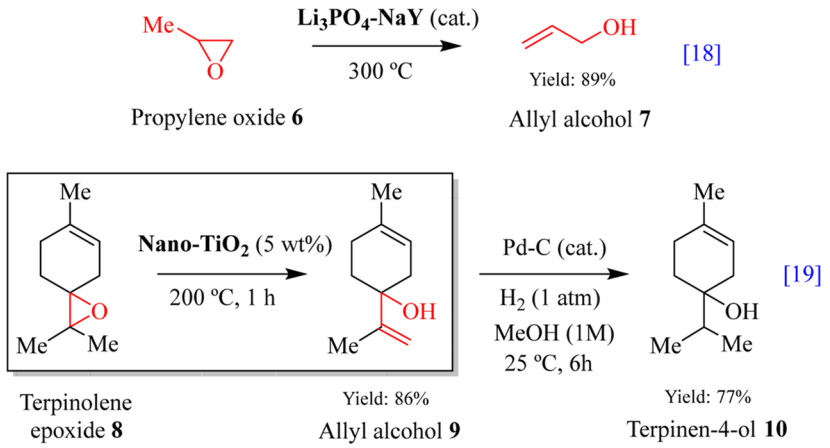
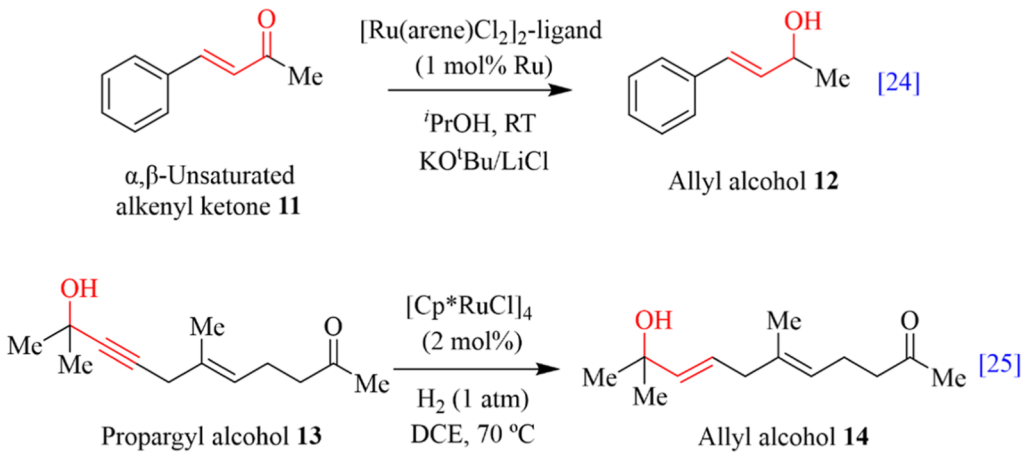
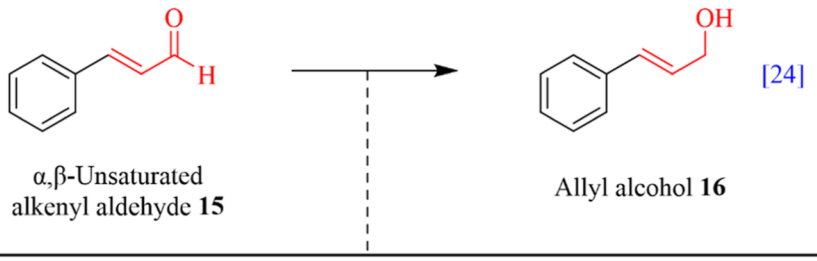


Figure 3. Synthesis of industrial allyl alcohols **7** and **9** after a solid−catalyzed isomerization reaction of epoxides.





Catalyst	Hydrogen source	Base	T (°C)
$Ru(PPh_3)Cl_2$ (0.04 mol%)	HCOOH	Et_3N	25
Rh catalyst (0.5 mol%)	HCOOH/THF	HCOONa	35
Zr zeolite β (77g/mol substr.)	^{i}PrOH	-	82
$HIrCl_2(Me_2SO)_3$ (4 mol%)	^{i}PrOH	-	83
Au/SiC (19 mol%)	^{i}PrOH	-	20
Pt/TiO_2 (1.5 mol%)	^{i}PrOH	-	25

Figure 4. Examples found in different reviews for the synthesis of allyl alcohols **12**, **14** and **16** by selective catalytic hydrogenation reaction of unsaturated alkyne and carbonyl compounds.[24,25]

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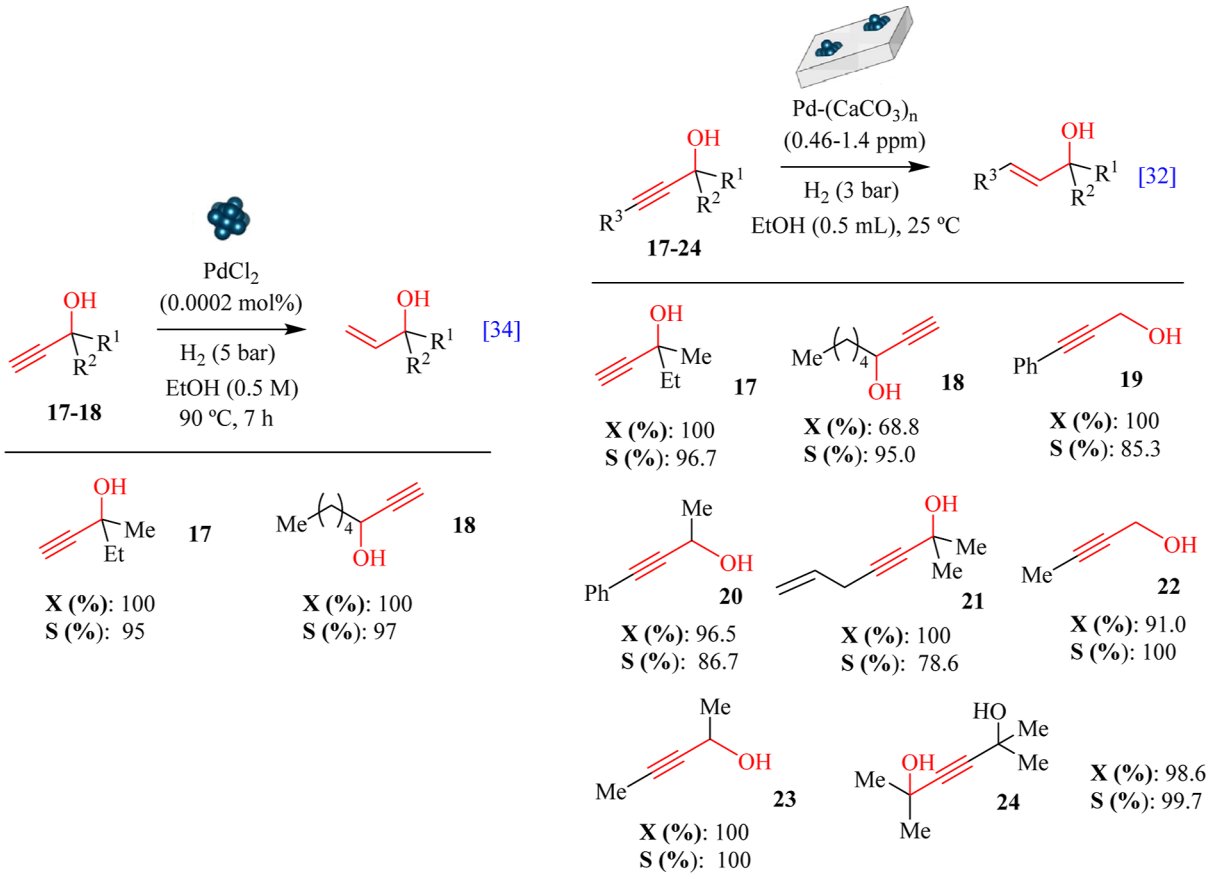

Figure 5. Selective semi−hydrogenation of propargyl alkynes **17**−**24** to allyl alcohols catalyzed by part−per−million amounts (ppm) of palladium(0) atoms either in solution or on calcium carbonate clusters. Selected examples.[32−34] X = conversion of the alkyne (starting material), S = selectivity toward alkene.

2. ACADEMIC RESEARCH ON THE SYNTHESIS OF ALLYL ALCOHOLS

2.1. Isomerization Reaction of Epoxides. The most common reaction to synthesize an allyl alcohol is the isomerization of the corresponding epoxide. This reaction has been extensively reviewed and can be carried out in an uncatalyzed way, i.e. through a metal or a base−induced β−elimination reaction of the epoxide,[10−12] or, most commonly, in a catalyzed fashion, with palladium as the preferred metal catalyst.[13−16] Figure 2 depicts the different approaches reviewed for the isomerization reaction of epoxides to allyl alcohols. The use of organocopper or strong bases reagents is highlighted and,[10−12] for instance, cyclopentene epoxide **1** or cyclohexene epoxide **4** are converted to the corresponding ketone and alcohol products **2**, **3** and **5**, even in an enantiomerically−enriched fashion. Regarding metal catalysts, gold, titania, cobalt and lanthanum, among others,[13−16] are able to catalyze the transformation of, for instance, enantiomerically−pure cyclohexene epoxide **4**, without loss of chirality.[16]

The use of a solid catalyst is generally preferred in industry not only for obvious practical and economic reasons but also from an operability point of view, since chemical processes with solid catalysts can be easily streamed in continuous reactors and easily monitored in−situ.[17] In this regard, a variety of solid catalysts have been reported for the isomerization of epoxides to the corresponding allyl alcohols and, not surprisingly, these catalytic solids have been directly studied for industrial allyl alcohols rather than laboratory compound models. Figure 3 shows that, for instance, zeolites have shown good catalytic activity as catalysts for the isomerization of propylene oxide **6** to allyl alcohol **7**,[18] and our group has shown that nanotitania catalyzes the isomerization of terpinolene epoxide **8** to the corresponding allyl alcohol **9**, to reach the commercial fragrance compound terpinen−4−ol **10**.[19] These results exemplify that simple and commercially available solid catalysts can catalyze the isomerization reaction of the epoxide to the desired allyl alcohol without the need of expensive and unrecoverable metal catalysts. A simple techno−economic analysis and life cycle assessment (LCA) would support the superiority of using these commercially available and recoverable solid catalysts, particularly the extremely cheap and innocuous titania, to perform the isomerization reaction compared to stoichiometric bases or metal catalysts in homogeneous phase. For that, the solid catalyst must be effective along multiple reaction cycles and, particularly, selective for the isomerization reaction. Indeed, the rational selection of the reaction conditions plays a key role to trigger the isomerization reaction vs other typical reactions of the epoxide in the presence of the solid catalyst, since, for instance, our group has also shown recently that both the zeolite and nanotitania solid catalysts can catalyze as well the hydration and hydroalkoxylation reaction of epoxides, rather than the isomerization reaction, under the appropriate reaction conditions.[20,21] These common competing reactions for epoxides have anyway vast applications in fine chemistry, such as the synthesis of menthoxypropanediol, a cooling agent which has recently reached the market to be used as a drug in the treatment for atopic skin.[22]

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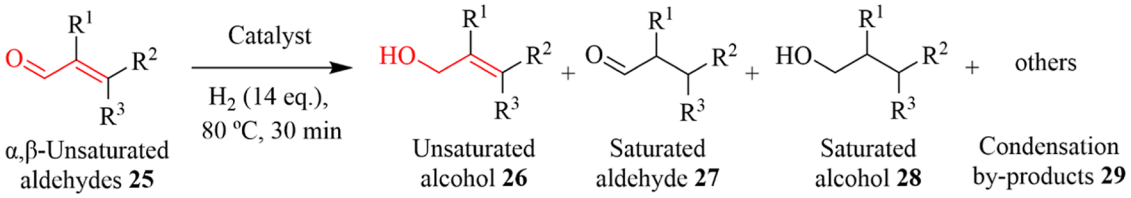

Starting material 25	Catalyst	Conv. 25 (%)	Select. (%)			
			26	27	28	29
Acrolein **25a** (R^1=R^2=R^3= H)	5% Cu/Al_2O_3	9.6	-	100	-	-
	5% Cu/Al_2O_3 modified*	1.1	46	54	-	-
Crotonaldehyde **25b** (R^1=R^3=H, R^2 =Me)	5% Cu/Al_2O_3	5.9	10	77	6	7
	5% Cu/Al_2O_3 modified*	1.7	43	41	-	16
2-Methylbut-2-enal **25c** (R^1=R^2=Me, R^3= H)	5% Cu/Al_2O_3	20.0	31	35	32	2
	5% Cu/Al_2O_3 modified*	6.0	41	9	34	16
3-Methylbut-2-enal **25d** (R^2=R^3=Me, R^1= H)	5% Cu/Al_2O_3	17.0	72	11	7	10
	5% Cu/Al_2O_3 modified*	19.0	79	2	-	19

* Modified with 1 μL of thiophene adsorbed at 210 °C. [39]

Figure 6. Solid−catalyzed hydrogenation reaction of unsaturated carbonyl compounds **25** for the synthesis of allyl alcohols **26** (**26a** is product **7**).

2.2. Hydrogenation Reaction of Unsaturated Alkyne and Carbonyl Precursors. A second methodology for the synthesis of allyl alcohols that can be considered as common as the isomerization reaction of epoxides is the hydrogenation of alkyne/carbonyl compounds, which include propargyl alcohols, *α,β*−unsaturated alkynyl ketones and esters, and *α,β*−unsaturated alkenyl carbonyl compounds (acrolein, crotonyl derivatives,···), among others. This strategy, abundantly commented in different reviews, as it occurs in the isomerization of epoxides, can also be uncatalyzed or catalyzed.[23,24] However, the literature widely explores the use of catalysts to activate the hydrogen−donor reactant (usually dihydrogen, H_2) and selectively hydrogenate the alkynyl and carbonyl functionalities without further hydrogenation of the alkene group.[25] Figure 4 shows some examples of this approach. For instance, cinnamyl ketone **11** is hydrogenated to the corresponding allyl alcohol **12** with isopropanol as hydride source under ruthenium catalysis, as the propargyl alcohol **13** to allyl alcohol **14** but with dihydrogen as hydride source. Cinnamaldehyde **15** can be converted to cinnamyl alcohol **16** with different hydrogen sources and catalysts.

Hydrogen autotransfer reactions have been reported and reviewed for the synthesis of allyl alcohols from alkyne−containing carbonyl and imine precursors,[26] through an intermolecular (enantioselective) carbonyl and imine reductive couplings catalyzed by nickel, cobalt, ruthenium, rhodium or iridium compounds,[27] and the resulting allyl alcohols can be used in target−oriented synthetic programs. For nickel, Ni(cod) and Ni(acac) can be employed as catalysts for a multicomponent coupling of carbonyl compounds with alkynes or 1,3−dienes with good regio−, stereo−, and enantioselectivity.[28] Another type of reductive coupling of alkynes and carbonyl compounds to give allyl alcohols is the cyclization reaction of alkynals with nickel and titanium oxametallacycle intermediates.[29] This reaction proceeds in an intramolecular fashion to give cyclic (enantioselective) allyl alcohols using, on one hand, organosilanes, organoboranes and organozincs as reducing agents, after an alkylative, arylative, or alkenylative cyclization reaction and on the other hand, H_2 as the reducing agent if rhodium complexes are used as catalysts. A particular case of homogeneous catalysis in the hydrogenation of unsaturated aldehydes (acroleins) to allyl alcohols is the use of air−stable and homogeneous gold nanoparticles, employing *tert*−butyl-(naphthalen−1−yl)phosphine oxide as a ligand.[30] Highly soluble nanoparticles with very small sizes (1.24 ± 0.16 nm) catalyze the hydrogenation of the unsaturated aldehydes, giving high conversions and chemoselectivity. The role of the ligand as a stabilizer is remarkable, since only the coordination mode adopted by the ligand on the nanoparticle surface enables the heterolytic hydrogenation mechanism.

The direct semi−hydrogenation reaction of propargyl alcohols with dihydrogen is also well described in the literature,[31] and our group has contributed to the field in the last years by developing more efficient palladium catalysts.[32−34] Beyond the well−known Lindlar's (palladium and lead supported on calcium carbonate) and BASF's colloidal ligand−protected Pd nanoparticles complex (also known as c−Pd/TiS) catalysts,[35,36] Figure 5 shows that the selective semi−hydrogenation of propargyl alkynes proceeds with part−per−million amounts (ppm) of palladium(0) atoms generated

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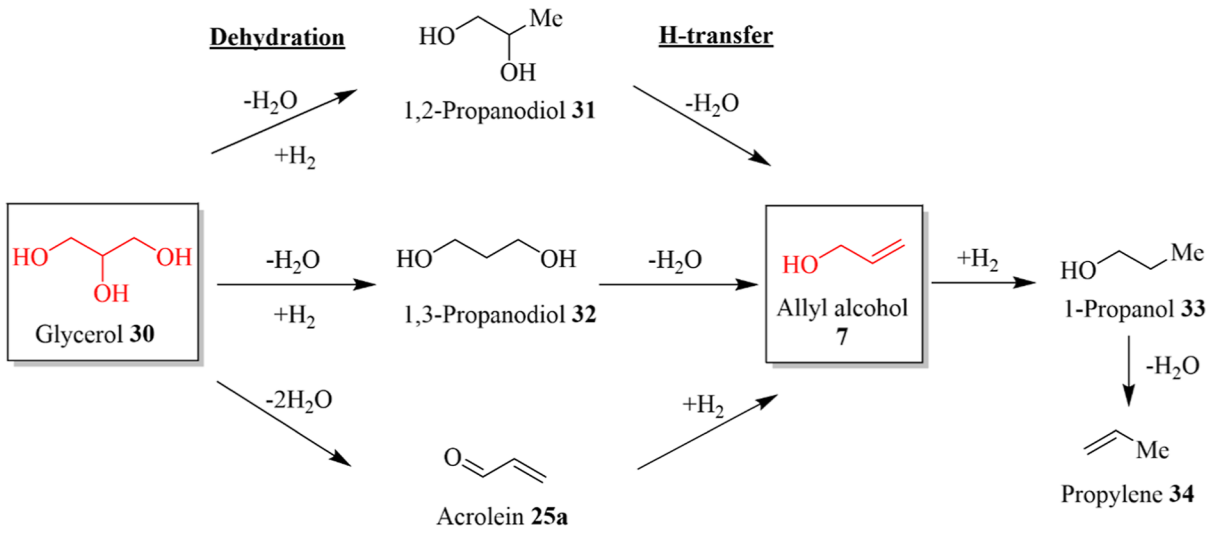

Catalyst	H donor	P (atm)	T (°C)	Yield (%)	
Fe_2O_3	Glycerol **30**	1	320	23	[46]
$NaReO_4$	Glycerol **30**	1	165	38	[46]
K/ZrO_2-FeO_x	Glycerol **30**	1	350	27	[47]
Rb/FeO_x-Al_2O_3	Glycerol **30**	1	340	13	[47]
K/Al_2O_3-ZrO_2-FeO_x	Glycerol **30**	1	350	25	[47]
Mo-V/HMMT	Glycerol **30**	1	320	22	[53]
CoFe alloy	Glycerol **30**	19	250	69	[58]

Figure 7. Different synthetic strategies reviewed for the catalytic hydrogenolysis reaction of glycerol **30** to allyl alcohol 7.[46]

in−situ from primary palladium salts (chloride, oxide, sulfate) in alcohol solutions, with extraordinarily high efficiency (turnover rate up to 735 s^{-1}) and yields (up to 99%).[34] The palladium(0) atoms stabilize themselves in solution after aggregation in ultrasmall sub−nanometer clusters, and these catalytically active species can be supported on calcium carbonate clusters to mimic the Lindlar's catalyst but without any lead or quinoline, in what is called the minimum catalytic unit for the semi−hydrogenation reaction,[32,37] in analogy with biochemistry terms.[38] A variety of allyl alcohols, for instance products **17**−**24** (selected examples) can be synthesized in this way. These simple catalytic systems decrease in, at least, 1 order of magnitude the economic costs associated with the Lindlar's catalyst, based on techno−economic and LCA analyses, since the Lindlar's catalyst requires resins to recover the palladium and, particularly, the lead metal lost during reaction, besides removing the quinoline additive after the hydrogenation process.

The use of solid catalysts for the synthesis of allyl alcohols from the corresponding unsaturated alkyne/carbonyl counterparts is also preferable from a sustainable industrial point of view, but it has not been widely reported in the literature, indeed, it is difficult to be found in any review. Some examples can be found in a general homogeneous/heterogeneous catalyst review,[29] where supported rhodium catalysts perform the cyclization reactions of alkynals with excellent levels of enantioselectivity to the chiral allyl alcohols, but beyond that, only particular examples can be found. For instance, Figure 6 shows that the hydrogenation of a series of α,β−unsaturated aldehydes and ketones **25** has been studied with 5% Cu on alumina modified or not with thiophene, and the results show that acrolein **25a**, crotonaldehyde **25b** and 2− or 3−methyl−2−butenal 25c−d generate the allyl alcohol products 26a−d (**26a** is allyl alcohol **7**) when increasing the amounts of thiophene, particularly for acrolein **25a** and crotonaldehyde **25b**, minimizing the amount of by−products **27**−**29**.[39] The origin of this selectivity is discussed in terms of geometric and electronic effects. Besides, a silver-supported silica catalyst has been reported to catalyze the hydrogenation of acrolein **25a** to allyl alcohol **7** with a 70% yield and 75% selectivity.[40] Palladium on carbon is a typical catalyst for the hydrogenation of crotonaldehyde−type substrates to the corresponding allyl alcohol, however, the reaction conditions have to be carefully controlled since, otherwise, the hydrogenation of the alkene instead of the aldehyde occurs.[41] This selectivity of supported palladium catalysts for the hydrogenation of α,β−unsaturated aldehydes to the allyl alcohol is enhanced if gold is added to the solid support, and even gold is able to catalyze this selective hydrogenation reaction on its own.[42] Although it could be thought that palladium and gold, as soft late−transition metals, would have more affinity for the alkene rather than the aldehyde group, the palladium/gold combination has shown enhanced hydrogenation activity for other oxygen−containing functionalities in different hydrogenation reactions.[43] In this sense, the substitution of more expensive late−by cheaper first−row

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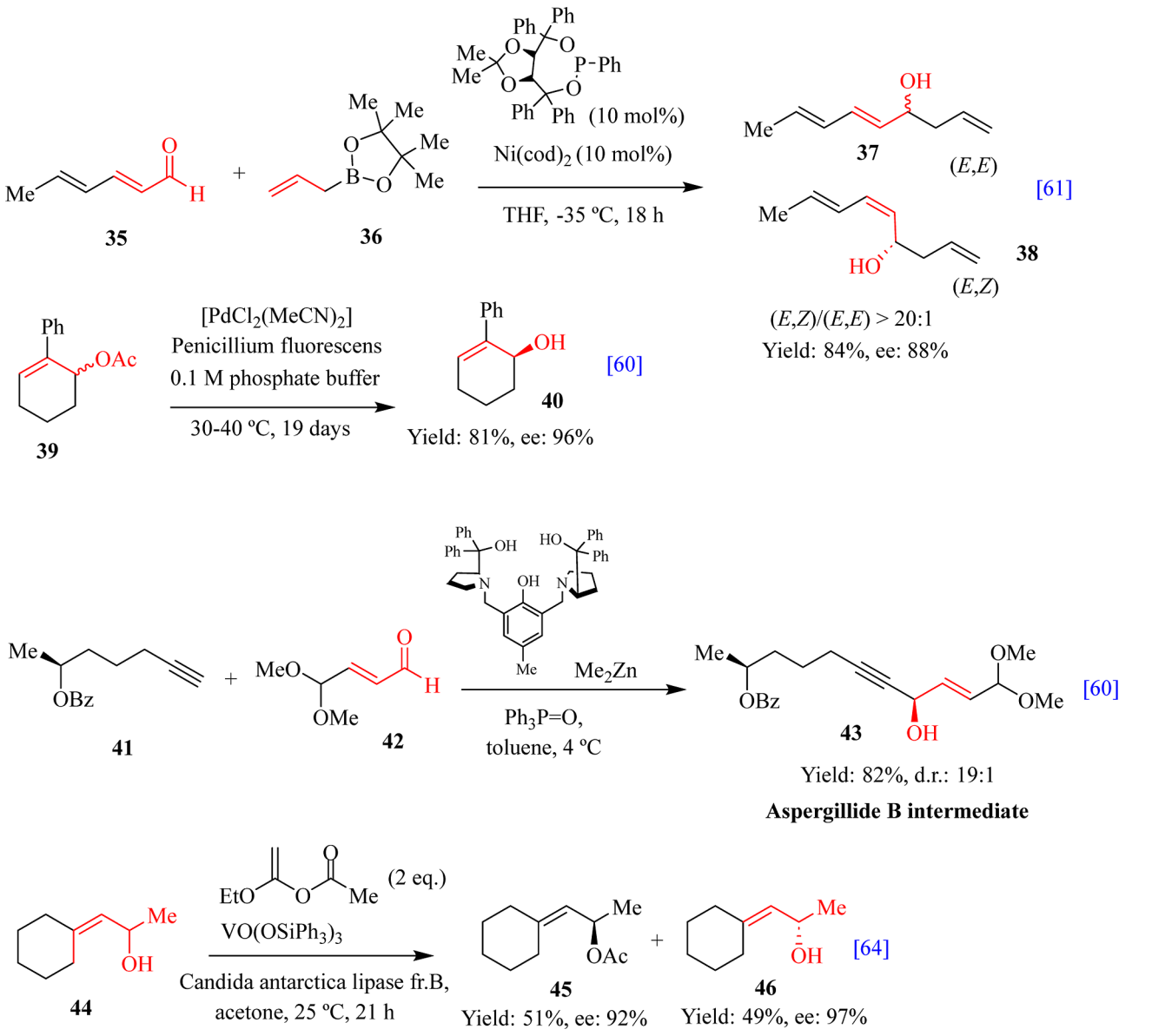

Figure 8. Different enantioselective synthesis of allyl alcohols **37**, **38**, **40**, **43** and **46**.

transition metals is also of interest to improve the costs and environmental burden of the hydrogenation process, and several alternative metal catalysts have been reported for this purpose. For example, it was early reported that a bimetallic Ni−Cu catalyst supported on aluminum phosphate catalyzed the hydrogenation of different propargyl alcohols (for instance 3−butyn−2−ol **22** and 2−methyl−3−butyn−2−ol **23**) at low reaction temperatures (<50 °C) and hydrogen pressures (3−7 bar).[44] In another representative early example, the selective hydrogenation of acrolein **25a** to allyl alcohol **7** was achieved with a cobalt supported on silica−alumina catalyst, to give a relatively high selectivity to allyl alcohol **7**, up to 33% at 50% conversion, in isopropanol at 500 °C for 1 h.[45]

2.3. Catalytic Hydrogenolysis Reaction from Glycerol. The use of renewable biomass provides a facile route to alleviate the shortage of fossil fuels and to reduce the emissions of CO_2, and glycerol is one of the most massive biomass resources. Therefore, it is not surprising that, as a C_3 compound, the direct transformation of glycerol **30** to allyl alcohol **7** has been extensively studied and reviewed in the last years.[46] It must be noticed here that this synthetic pathway only achieves the simplest allyl alcohol **7** and not any other allyl alcohol derivatives, and requires a selective catalyst to circumvent the formation of other C_3 products such as 1,2−propanediol **31**, 1,3−propanediol **32**, 1−propanol **33** and propylene **34**, as it is shown in Figure 7.

A techno−economic analysis of the synthesis of allyl alcohol **7** from glycerol **30** reveals that the investment required for glycerol valorization processes in a biorefinery, based on the Guthrie, Taylor, and Aspen capital cost estimation methods, makes glycerol carbonate as the dominant product to maximize the profitability with respect to the glycerol utilized, but leaves allyl alcohol **7** (and also 1,2-propanediol **31**) as potential target compounds to be included in the glycerol biorefinery product mix if a further decrease of the environmental impact is accomplished.[8] These data support the industrial viability at the short-term of the glycerol−to−ally alcohol route.

Liquid−and vapor−phase reactions can be employed for the catalytic hydrogenolysis of glycerol **30**, in the presence of a heterogeneous solid catalyst. For example, the conversion of **30**

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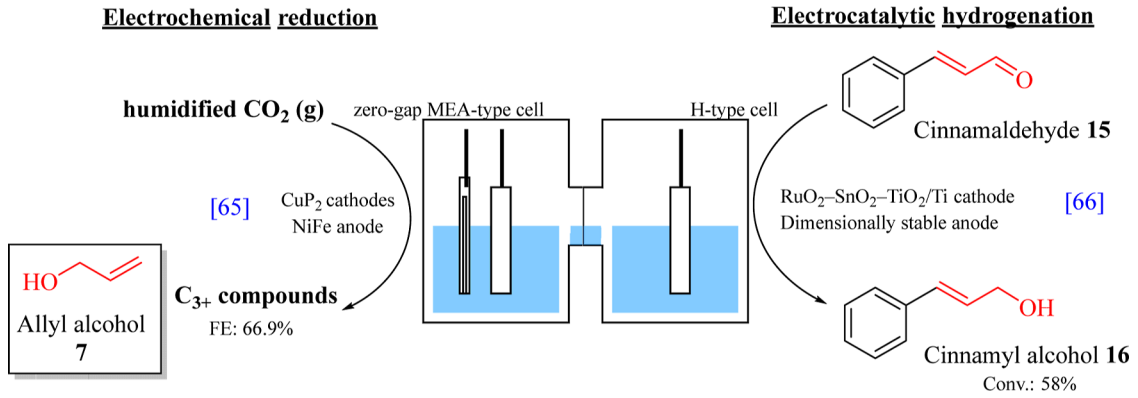

Figure 9. Electrocatalytic synthesis of allylic alcohols. (Left): CO_2 electroreduction on a phosphorus-rich Cu catalyst producing allyl alcohol **7** within the C_{3+} compounds. (Right): electrocatalytic hydrogenation of cinnamaldehyde **15** to cinnamyl alcohol **16** on RuO_2–SnO_2–TiO_2/Ti electrode, illustrating selective C═O hydrogenation over C═C.

into allyl alcohol **7** has been reported for potassium–supported zirconia–iron oxide catalysts,[47] in a fixed–bed flow reactor at 623 K under atmospheric pressure. Not only neat but also crude glycerol **30** from the waste solution of biodiesel production was used, and different alkali metals, from sodium to cesium, can be supported on the zirconia–iron oxide solid to give up to 27% yield of allyl alcohol **7**. It was suggested that the acid rather than the basic sites of the solid catalyst are responsible for the glycerol dehydration, which proceeds through a hydrogen transfer mechanism since any dihydrogen is not added to the system. Although formic acid is formed during the reaction, the hydrogen autotransfer reaction pathway resembles that of epoxides when isomerizing to allyl alcohols (see Section 2.1 above), which suggests that the epoxide of glycerol (glycidol) may be an intermediate for the hydrolysis reaction of glycerol **30** to allyl alcohol **7**. Indeed, the gas–phase conversion of glycerol **30** into glycidol has been reported with an acid Socony Mobil (HZSM)–5 zeolite catalyst modified with cesium, in a packed–bed continuous flow reactor at 350 °C reaction temperature under atmospheric pressure, to give a 40% yield.[48,49] Again, the relatively high selectivity and stability of the solid catalyst was attributed to the presence of a suitable amount of basic sites, which is a common strategy to control the reactivity and selectivity of zeolites in organic reactions.[50−52] Nevertheless, glycidol is not necessarily the intermediate during the hydrogenolysis of glycerol **30** to allyl alcohol **7**, since it has been reported that molybdenum–vanadium oxides supported on acid–modified montmorillonite catalyze the gas–phase hydrogenolysis of **30** to **7** with acrolein **25a** as a key intermediate.[53] As it occurs in the zirconia–iron oxide and HZSM–5 catalysts, the acidic sites facilitate the dehydration reaction, to give acrolein **25a** with ∼74% selectivity, to achieve in this way a 22% yield of allyl alcohol **7** at 320 °C. Low–valence vanadium species are proposed to mediate the hydrogen transfer reaction of **25a**, with water playing a key role as a hydride donor from the unsaturated aldehyde to allyl alcohol **7**. Other works confirm the high catalytic activity of zirconium oxides and HZMS–5 catalysts for the conversion of glycerol **30** and other alcohols to dehydrated products.[54−57] Nevertheless, the direct transformation of **30** to allyl alcohol **7** can also occur on completely different solid catalysts to those above commented and, for instance, cobalt–iron alloys, prepared after calcination and reduction of a zeolitic imidazolate cobalt–iron framework (CoFe–ZIF) precursor, catalyze the formation of **7** from **30** in 90% conversion and 69% selectivity at 250 °C and 2 MPa pressure.[58]

We will comment ahead (see outlook, Section 4) about other reports on the transformation of glycerol **30** to allyl alcohol **7**, contextualized in the new lines of research proposed to substitute petrochemical-based processes by renewable-based processes.

2.4. Enantioselective Synthesis of Allyl Alcohols. Secondary and tertiary allyl alcohols present a stereogenic center which can be enantioselectively formed during the preparation of the allyl alcohol, in fact, they represent an important and highly versatile class of chiral building blocks for organic synthesis. One example has already been shown above, in Figure 2. Two methodologies for the preparation of chiral allyl alcohols apart from the methods mentioned above are essentially found in the literature, in order to induce the required chirality to the allyl alcohol product.[23,28,59] These methods are the direct catalytic addition of allyl surrogates to carbonyl compounds with chiral catalysts and the dynamic resolution of racemic mixtures,[60] both shown in Figure 8. For the former, specific enantioselective allylation methodologies have been reported and, for instance, the direct catalytic asymmetric allylation of carbonyl compounds such as **35** with organoboronates **36** has been extensively reviewed, to give products **37** and **38**.[61] This methodology allows the preparation of chiral building blocks based on allyl alcohols for the synthesis of natural products and pharmaceuticals. The combination of a palladium catalyst with triethylborane has been extensively employed and reviewed for the transformation of allyl acetates such as **39** to allyl alcohols **40**, by electrophilic allylation reaction of a plethora or electrophiles, including aldehydes.[62] This activation can be amphiphilic, and the above-commented palladium catalyst, also combined with diethyl zinc, effects not only the generation of allyl anions but also of allyl cations, as for reactants **41** and **42** to the allyl alcohol product **43**.[63] Regarding dynamic resolutions, enantiomeric pure allyl alcohols can be obtained by the combined use of lipases and vanadium oxidesafter the 1,3–transposition of the allyl alcohol **44** to the thermodynamic mixture of the two regioisomers,[64] and highly stereoselective and chemoselective esterification with the lipase catalyst, to give products **45** and **46**.

2.5. Electrocatalytic Synthesis of Allyl Alcohols. Electrocatalysis has recently emerged as a complementary and potentially sustainable route to access allylic alcohols, although the number of reports remains limited compared to conventional thermocatalytic processes. In general, two main approaches can be distinguished: the direct electrochemical

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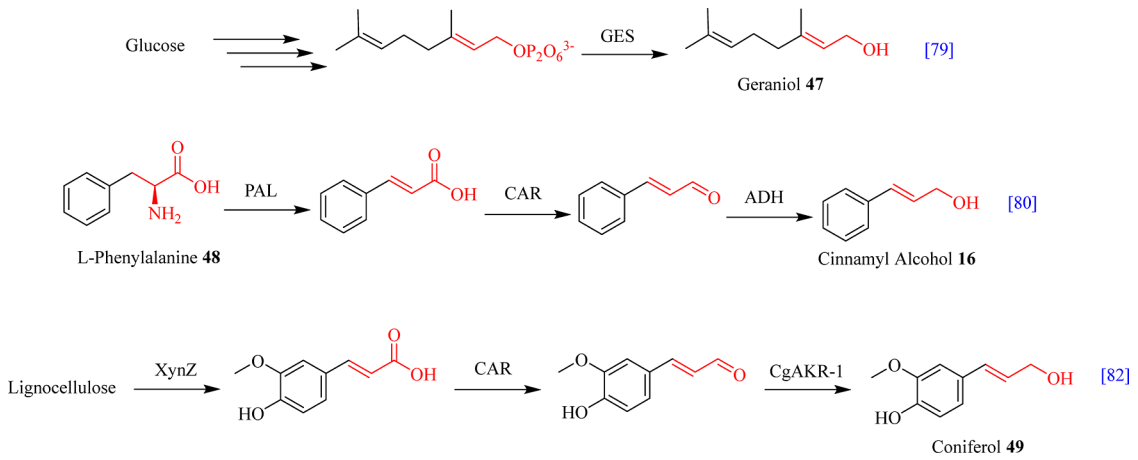

Figure 10. Representative biocatalytic routes to allylic alcohols from renewable feedstocks. GES = geraniol synthase, PAL = phenylalanine ammonia lyase, CAR = carboxylic acid reductase, ADH = alcohol dehydrogenase, XynZ = chimeric xylanase, CgAKR-1 = aldo-keto reductase.

reduction of CO_2 into C_3 oxygenates and the electrocatalytic hydrogenation of α,β−unsaturated aldehydes or ketones, as shown in Figure 9.

A representative example of the first approach employs a phosphorus−rich copper catalyst that converts CO_2 at industrially relevant current densities (-1100 mA·cm^{-2}) into liquid C_{3+} products with a Faradaic efficiency (FE) of 66.9%, among which allyl alcohol **7** is identified as one of the main products.[65] Although still at a very low technology readiness level (TRL <3), these results demonstrate that renewable carbon sources and electricity can be coupled to generate allylic alcohols under continuous-flow electrochemical conditions.[65]

The second strategy involves the electrocatalytic hydrogenation (ECH) of α,β−unsaturated carbonyl compounds. Cinnamaldehyde **15** is commonly used as a model substrate to selectively afford cinnamyl alcohol **16** under mild aqueous conditions, and electrodes based on Pt−MoO_3/C, RuO_2−SnO_2−TiO_2/Ti or defect−rich MoS_2 favor the hydrogenation of the carbonyl group over the C═C bond, typically reaching Faradaic efficiencies in the 50−80% range.[66−68] Similarly, crotonaldehyde **25b** can be reduced to crotyl alcohol at suitably engineered cathodes, confirming that ECH can be tuned to generate different allylic alcohols depending on the substrate.[69] Overall, recent overviews delineate both the selectivity handles and the remaining barriers to scale up these electrochemical routes.[70]

2.6. Photocatalytic and Photochemical Synthesis of Allyl Alcohols. Photocatalysis provides a complementary route to access allylic alcohols under very mild conditions, harnessing light energy to drive transfer-hydrogenation steps that selectively reduce C═O functionalities while preserving C═C bonds. Early advances were driven by metal-modified photocatalysts, especially plasmonic designs on wide-band gap semiconductors such as TiO_2 and SiC, which illustrate the chemoselectivity attainable under visible light. Thus, **Au/SiC** delivers quantitative selectivity to cinnamyl alcohol 16 from cinnamaldehyde 15 at 20 °C using i-PrOH as hydrogen source, with localized surface plasmon resonance of Au nanoparticles and charge transfer across the SiC/Au interface, identified as the origins of activity.[71] In a similar vein, **Au/TiO_2** and **Au/Pt−TiO_2** couple plasmonic absorption with semiconductor charge separation to afford high selectivity to allylic alcohols in cinnamaldehyde reduction under visible light, reinforcing the generality of this design principle.[72] Beyond transfer-hydrogenation, visible-light $E \rightarrow Z$ photoisomerization has also enabled the selective synthesis of *Z*-cinnamyl alcohols and ethers, highlighting the mechanistic diversity accessible within photocatalytic routes to allylic alcohols.[73]

Subsequent studies with oxide-only TiO_2 variants (amorphous or defect-engineered) showed that high chemoselectivity can also be achieved without noble metals, particularly for the transfer hydrogenation of α,β-unsaturated aldehydes with secondary-alcohol donors at room temperature. In these systems, the competitive adsorption of water and carbonyl species, together with the surface population of hydrogen equivalents, governs the balance between C═O and C═C reduction pathways.[74] Complementarily, earth-abundant Cu(I) cluster-based polymer photocatalysts achieve chemoselective visible-light transfer hydrogenation of α,β-unsaturated carbonyls, extending beyond TiO_2 and noble-metal designs.[75]

Broader overviews of TiO_2-mediated photocatalytic transfer hydrogenation compile principles, common H-donors and substrate scope, and include cases in which propargyl alcohols are semihydrogenated to the corresponding allylic alcohols under irradiation.[76] From a process standpoint, recent analyses of photocatalytic transfer hydrogenation using water-derived hydrogen equivalents outline opportunities to reduce sacrificial-donor usage and highlight reactor/illumination variables that currently limit space−time yields.[77] Recent demonstrations in continuous-flow photoreactors suggest a practical route to improve photon economy and space−time yield while facilitating scale-up, although long-term catalyst stability remains a major bottleneck. Importantly, these operations can be conducted under solar irradiation or LED lighting powered by renewable electricity.[77] Overall, photocatalytic strategies demonstrate that light-driven redox processes can achieve both high selectivity and reduced energy input for allylic alcohol synthesis. However, the limited long-term catalytic stability and reactor productivity indicate that these systems must evolve from proof-of-concept designs toward integrated solar or LED-assisted flow operations.

2.7. Biocatalytic and Biorefinery Approaches. Biocatalysis offers unmatched selectivity and operates under environmentally benign conditions, making it an attractive strategy for allylic alcohol synthesis. Beyond the glycerol platform, biobased routes enable the production of a broad range of allylic alcohols through fermentative pathways using engineered microorganisms, multienzyme cascades, or hybrid

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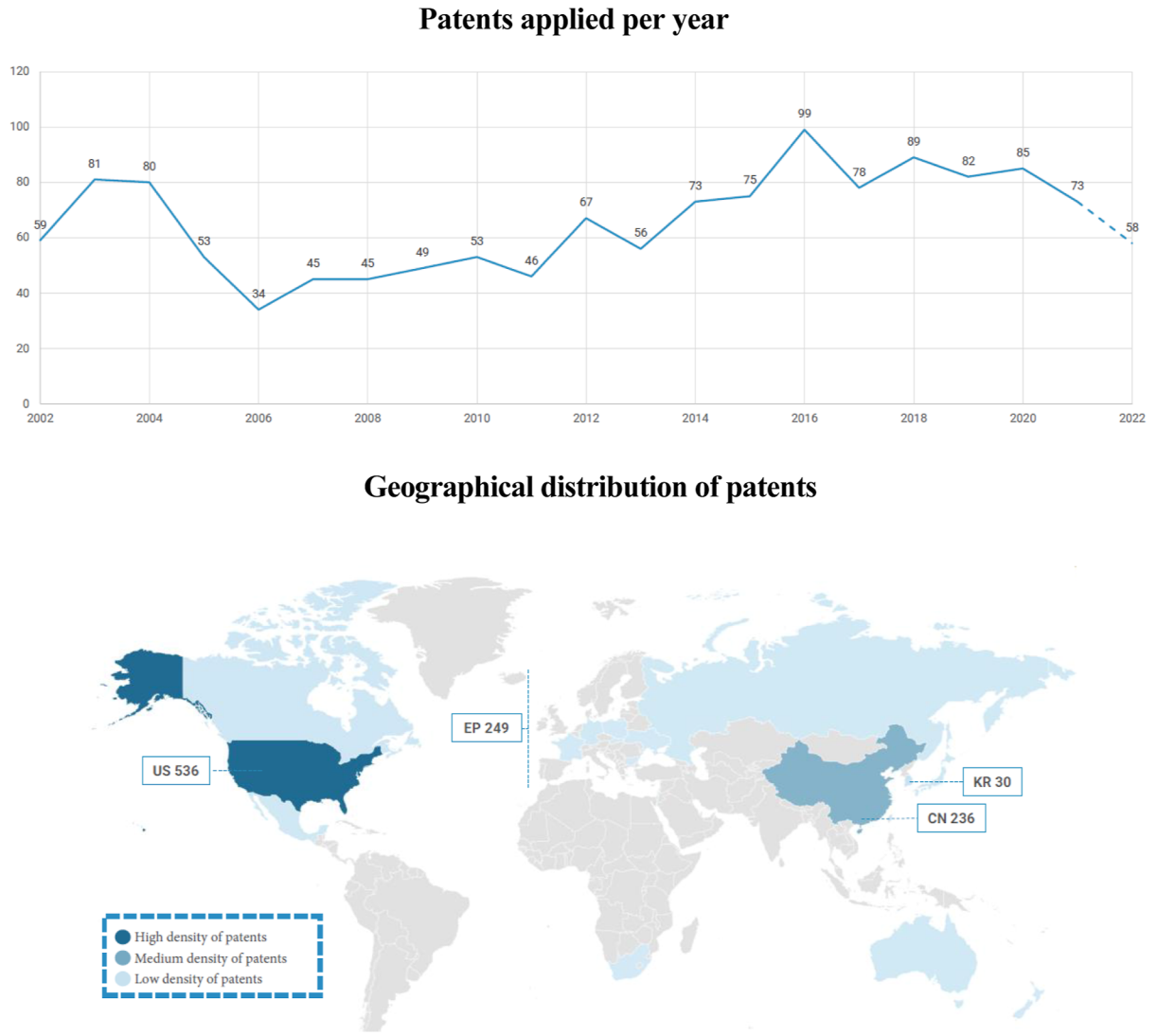

Figure 11. Top: number of patents registered per year for the patent search with the relevant terms "allyl alcohol" and "production/preparation/manufacture/synthesis or method" in the title, abstract or claims, using the public database WIPO Patentscope, EPO Espacenet, USPTO Patent search, Google Patent and SPTO. Bottom: number of patents per country.

chemoenzymatic sequences that convert renewable carbon feedstocks into functionalized allylic intermediates.[78−82] As illustrated in Figure 10, representative examples encompass microbial and enzymatic routes to **geraniol 47** from glucose,[79] cinnamyl alcohol 16 from L-phenylalanine **48**,[80] and coniferyl alcohol 49 from lignocellulosic biomass.[82] Each transformation relies on tailored enzyme cascades that integrate synthases, reductases, and dehydrogenases operating in aqueous media, exemplifying how biorefineries can valorize sugars, amino acids, and lignin-derived aromatics into allylic alcohols or their immediate precursors with high atom efficiency and minimal waste generation. Although such systems remain at low technology readiness levels, they demonstrate the growing convergence of biotechnology and catalysis in advancing renewable pathways to allylic alcohols.

Although a one-step enzymatic conversion of glycerol **30** into allyl alcohol **7** has not yet been reported, biological precedents indicate that allylic motifs can be enzymatically manipulated. For example, the iron−sulfur enzyme IspH in the methylerythritol phosphate pathway performs reductive dehydroxylations on allylic-type intermediates, motivating enzyme-engineering efforts toward this product family.[83]

From a process standpoint, selective chemo-enzymatic resolution and refinement are already valuable for stereocontrol and late-stage selectivity in allylic alcohols. For instance, lipase-catalyzed dynamic kinetic resolution (DKR) coupled with mild vanadium-oxide racemization has been applied to benzylic allylic alcohols to deliver highly enantioenriched products under benign conditions, illustrating the complementarity between enzymatic selectivity and heterogeneous catalysis.[64]

From a feedstock perspective, biobased platforms, including crude glycerol **30** (see Section 2.3),[84] 3-hydroxypropionaldehyde (3-HPA), lactic acid, and itaconic acid, are established biorefinery building blocks.[85−87] These streams can be funneled to allylic intermediates (e.g., acrolein from 3-HPA) and, after short chemoselective C═O hydrogenation of α,β-unsaturated carbonyls (e.g., aldehydes), to the corresponding allylic alcohols.[88]

Looking ahead, priority directions are to expand enzyme toolkits capable of allylic deoxygenation and selective reduction, increasing space−time yields and catalyst lifetime in aqueous

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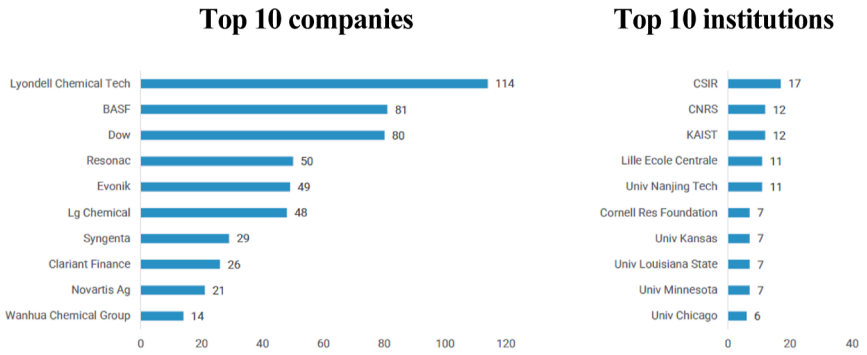

Figure 12. Number of patents per chemical company (left) or research institute (right), in the period 2002−2022, after a patent search with the relevant terms "allyl alcohol" and "production/preparation/manufacture/synthesis or method" in the title, abstract or claims (see Figure 11).

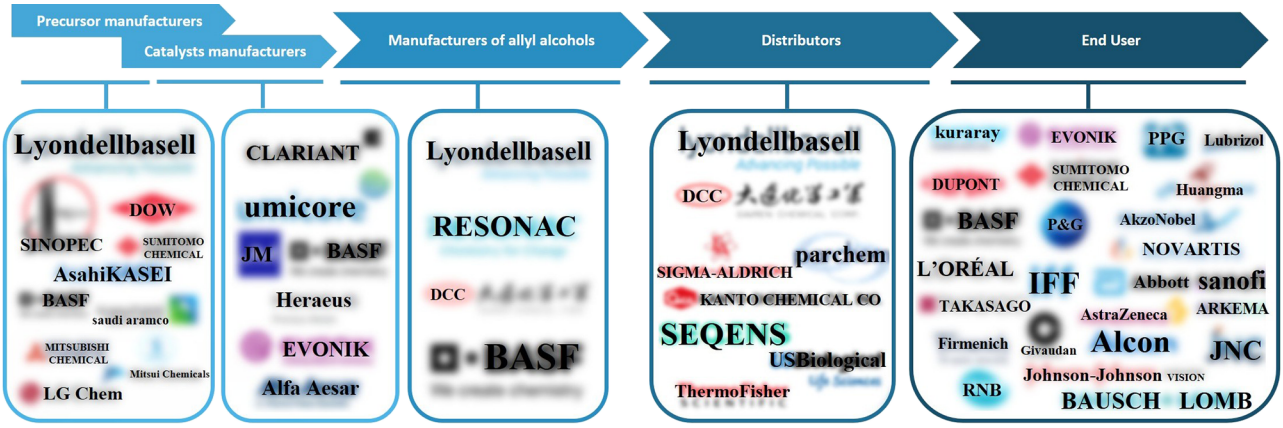

Figure 13. A potential value chain of the allyl alcohol market, with some of the main companies involved.

media to process-relevant levels, and to merging biobased platforms with short thermo- or electrocatalytic segments in continuous operation. Collectively, these advances would raise the technology readiness level of biocatalytic routes while preserving the selectivity and sustainability advantages that make biocatalysis a key enabler for future allylic alcohol manufacturing.

3. INDUSTRIAL PRODUCTION OF ALLYL ALCOHOLS

The large-scale manufacture of allyl alcohols is currently based on petrochemical technologies derived from propylene **34**, mainly through epoxide isomerization, allyl acetate hydrolysis, and acrolein **25a** hydrogenation. This section reviews the main industrial processes, patent landscape, and corporate actors involved in their production and use. While the focus remains on established petrochemical routes, it is worth noting that emerging biocatalytic and biorefinery routes (Section 2.7) are gaining attention as long-term sustainable alternatives that may complement conventional industrial pathways.

3.1. Patents and Analysis. A patent analysis over the last 20 years has been carried out in order to evaluate the state−of−the−art of the intellectual property protection with respect to the use and manufacture of allyl alcohols, in order to assess the interest of research institutions and companies in the development of new technologies. The patent databases used for this search are international and publicly accessible: WIPO Patentscope, EPO Espacenet, USPTO Patent search, Google Patents and SPTO, including the term "allyl alcohol" together with the terms "production/preparation/manufacture/synthesis or method" in the title, abstract or claims. In addition, the search was conducted under the CPC C07 term,[89] thus referring to organic chemistry, with the aim of reducing the noise generated in the search. A total of 1380 patents have been identified and, as Figure 11 shows, the trend of these publications in the period 2002−2022 is stable, an expected behavior for chemicals with stabilized markets (see the explanation for this in the introduction). Figure 11 also shows the geographical distribution of these patents, where the United States is the region which comprises the largest number of published patents, followed by the European Union and China.

The highest number of patents comes from manufacturing companies rather than research centers (including universities), as can be seen in Figure 12. The number of patents regarding the synthesis of allyl alcohols filed by chemical companies is 1 order of magnitude higher than research institutions, which clearly indicates a mismatch between industry and academy, thus encouraging the academic research community to work on this topic. Among the patenting companies, it is possible to establish some profiles according to their industrial activity. For instance, certain sectors such as the pharmaceutical or cosmetic industry appear more prominently in the patent study, and, remarkably, companies oriented to the production of catalysts are also very actively involved in the development of new solutions to optimize the manufacture of allyl alcohols. It is important to differentiate the companies with patents dedicated to the use of allyl alcohols rather than their manufacture, since the latter constitutes the minority. In other words, there are fewer companies producing allyl alcohols for their direct selling that for their use as intermediates, and this will be properly detailed in the value chain analysis (see Section 3.2).

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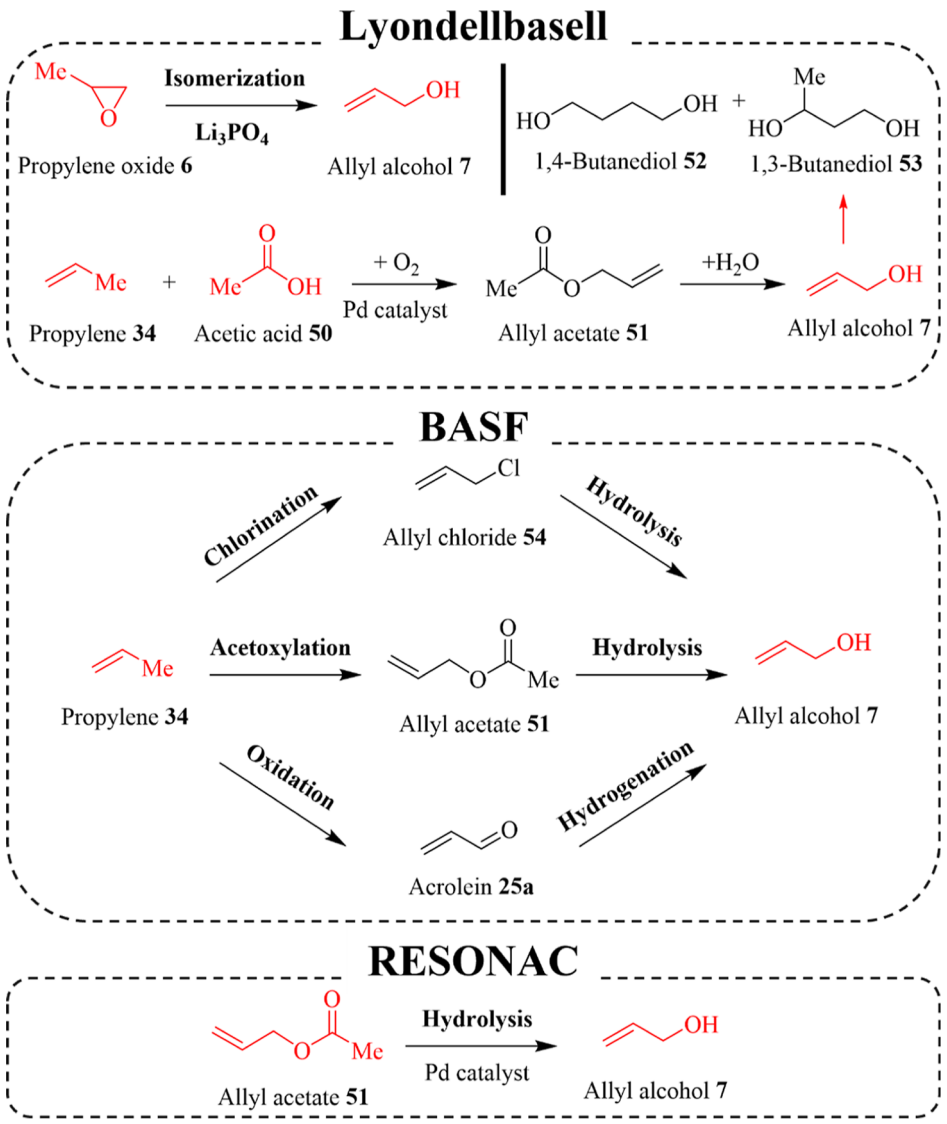

Figure 14. Representative industrial processes for the manufacture of allyl alcohol 7.

3.2. Profile of the Chemical Companies and the Value Chain. The patent analysis above reveals that the profile of the chemical companies involved in the managing of marketable allyl alcohols, either as final manufacturers or intermediates for other products, generally corresponds to a multinational dedicated to the production of a wide variety of chemical products, without focusing their activity exclusively on the manufacture of allyl alcohols. Among these companies, it is possible to identify players of great relevance in the sector such as BASF, Dow, or LyondellBasell, but it is also possible to detect the presence of catalyst manufacturers, pharmaceutical companies and companies specialized in cosmetics. While catalyst manufacturers offer solutions aimed at improving the chemical process of the allyl alcohol, pharmaceutical and cosmetic companies use allyl alcohols as raw material for the synthesis of their final products, such as vitamins, lenses, creams, medicines and fragrances, among others.

Figure 13 shows some of the main companies and their estimated position in the market value chain of allyl alcohols. This value chain is presented in a simplified way, divided into the following stages: manufacturers of precursors together with catalyst developers, manufacturers of allyl alcohols, distributors and end users. In addition, some examples of companies working in the various steps of the chain are shown to provide an overview of their business activities. The aim here is to illustrate the value that obtaining allyl alcohols can bring to all levels of the commercial chain and which of these activities give a greater commercial impact on the allyl alcohol market.

The raw materials for obtaining allyl alcohol 7 come mainly from petroleum derivatives and they mostly include propylene oxide **6**, acrolein **25a** and propylene **34**. These data strikingly contrast with the conveniency of more sustainable production methods, such as those starting from glycerol **30**. However, as a 1,3−bifunctional structural compound, allyl alcohols are often not purified for storage and selling but the synthesis is extended to produce more complex compounds, with greater added value. This makes one think that the current research of bioavailable sources such as glycerol **30** should be more focused on the subsequent products from allyl alcohols that the very same allyl alcohols. Indeed, the latter are prone to rearrangement and migration reactions, which include the semipinacol, Meinwald and neophyl rearrangements, among others, to generate the corresponding carbonyl compounds.[90,91] The main approaches to prepare these carbonyl compounds from allyl alcohols have

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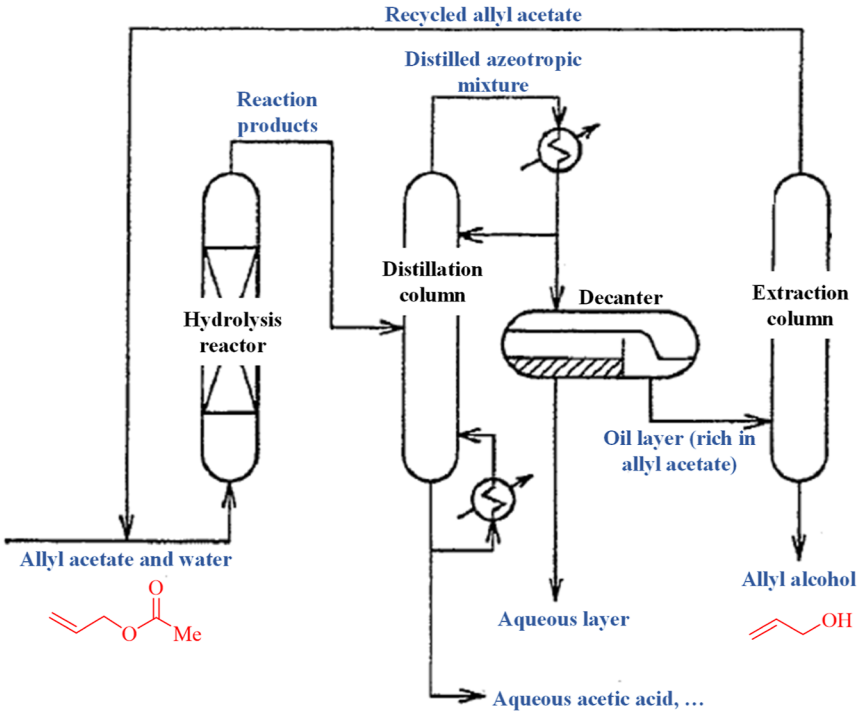

Figure 15. Simplified flow diagram for the hydrolysis of allyl acetate 51 to allyl alcohol 7. Process sequence based on Showa Denko's patent US 8083903 B2.[96]

been reviewed in the literature and they are all catalytic, employing late−transition metals such as, for example, gold or rhenium.[92−95] Rhenium catalyzes the [1,3]−transposition not only of allyl alcohols but also of their silyl ether derivatives, which occurs via [3,3]−sigmatropic rearrangement with a high oxidation state oxometal complex, with application in natural product synthesis. Therefore, the direct transformation of glycerol **30** in these products should be considered. The transformation of allyl alcohols also occurs at the biological level, and the complete dehydro−oxygenation reaction to alkenes has been reviewed for the IspH protein catalyst, which catalyzes the reductive dehydroxylation of the allyl alcohol through a biosynthetic pathway to give the isoprenoid compounds.[83]

In any case, the petrochemical manufacture of propylene oxide **6**, acrolein **25a** and propylene **34**, i.e. the precursors of allyl alcohol **7**, is effected by huge producer companies, thus **7** is also produced by the same companies, which must fulfill the synthetic needs of the market. The catalysts used in these processes generally belong to the platinum group of metals (PGM), such as palladium or ruthenium, which entails large associated operating costs, being of relevance their optimization. The synthetic methods widely vary between the manufacturing companies, from the isomerization of propylene oxide **6** to the reaction of propylene **34** with acetic acid **50**, among others, and the main companies and processes worldwide include.

- LyondellBasell (Netherlands, turnover > $50,000M, number of employees: >10,000): The production process for allyl alcohol **7**, as listed on its website and shown in Figure 14, consists in the isomerization of propylene oxide **6** with a lithium phosphate catalyst at high temperatures. However, the company possesses other patented processes, such as the reaction of propylene **34**, acetic acid **50** and oxygen with palladium catalysts, with the intermediacy of allyl acetate 51. In any case, the synthesis of allyl alcohol **7** relies on a previous oxidative process of propylene **34**. The company highlights the importance of allyl alcohol **7** in the internal production processes to synthesize other valuable products such as 1,4−butanediol **52** and 1,3−butanediol **53**. This company also offers allyl alcohols separately.
- BASF (Germany, turnover: > $50,000M, number of employees: >10,000): In an overall flowchart, BASF includes the production of allyl alcohol **7** by three different routes: (1) allyl chloride **54** hydrolysis, (2) allyl acetate **51** hydrolysis and (3) acrolein **25a** hydrogenation. It has not been possible to find information on the catalysts used for the hydrogenation process. As it can be seen in Figure 14, these processes are completely different to that of LyondellBasell and rely on a previous functionalization of propylene **34**, not necessarily oxidative, and a final hydrolysis or hydrogenation of the C_3 intermediate. In this way, the company manufactures different allyl alcohols, which are employed as raw materials for the production of their product Pluriol (a polyalkylene glycol), present in the formulation of detergents and cleaning agents.
- Resonac (Japan, turnover: > $20,000M; number of employees: >10,000): the Resonac process diagrams list the production of allyl alcohols after hydrolysis of allyl acetate **51** (see Figure 14), which is in turn produced in a process catalyzed by palladium. A simplified flow diagram of this hydrolysis route, illustrating the main reaction, distillation, and separation steps, is shown in Figure 15. Resonac's olefins segment covers 34.3% of its activity and includes the manufacture of allyl alcohols. The company highlights that the sale price of these compounds has increased in the last years, so their relevance in the markets. They also sell allyl alcohols to other companies and distributors.

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Taken these three companies as references, it can be seen that the production of allyl alcohol **7** follows different pathways depending on the companies' raw materials availability. The isomerization reaction of epoxides takes the lead if an efficient epoxidation process is operated within the company and further functionalization of the epoxide is not required. However, the functionalization−hydrolysis/hydrogenation route is preferred if the selected technology can skip the epoxidation reaction or the further opening of the epoxide is economically acceptable. These synthetic strategies for the simplest ally alcohol **7** is extensible, with the appropriate modifications, to the rest of the allyl alcohols.

The second step in the value chain of allyl alcohols comprises the distributors (see Figure 13), and it is possible to identify two main profiles. In the first profile, alcohol manufacturing companies with their own distribution services are found, from which they distribute the product through Web sites. On the other hand, the second profile is composed by companies dedicated exclusively to the distribution of different chemicals, and those include allyl alcohols. These companies can provide the material in different purities and volumes, either for industrial use (for which they establish agreements with large producers) or for use in research laboratories (smaller quantities are necessary and can be manufactured in their own laboratories). Due to the wide range of applications in which allyl alcohols can be used, it is also possible to identify different profiles within end users (see Figure 13). For instance, some chemical companies use the allyl alcohol as the main element of their formulations, however, other companies use the allyl alcohol as an additive for the manufacturing of other compounds.

3.3. The Issue of Palladium Catalysts for the Allyl Alcohol Production. Palladium is the most common catalytic metal for the industrial synthesis of allyl alcohols, appearing in different processes, as has been shown above. Since the use of palladium has spread widely in different markets, as it is not only used in catalysis but also in three−way combustion exhausts, fuel cells, jewelry or electronic components, as well as in dental applications or hydrogen storage, the market value of palladium has sharply increased in recent years, as reflected in the increasing price shown in Figure 16.[97]

It is estimated that 85% of palladium is used to manufacture combustion vehicles. In China, the record for the use of palladium in the sector has been reached in the last years, with >70 tons of palladium consumed per year. Besides, factors such as the war in Ukraine or the lack of semiconductors have caused instabilities in the precious metals market, also affecting palladium over the last years. Russia is positioned as one of the main producers of palladium (together with South Africa, they comprise 75% of production), so promoting chemical processes that use less palladium will be clearly beneficial for the chemical industry. The European Union has considered palladium as a critical raw material since 2011, so actions and projects to reduce its consumption or encourage its recycling are promoted. Besides, regulatory actions in the mining sector (this area of activity is also responsible for between 4 and 7% of global greenhouse gas emissions) can increase even more the cost of palladium obtained. Therefore, any new technology which enables the decrease of the palladium catalyst amount or substitution with cheaper, more available and environmentally benign metal catalysts, would significantly impact on the synthesis of allyl alcohols.

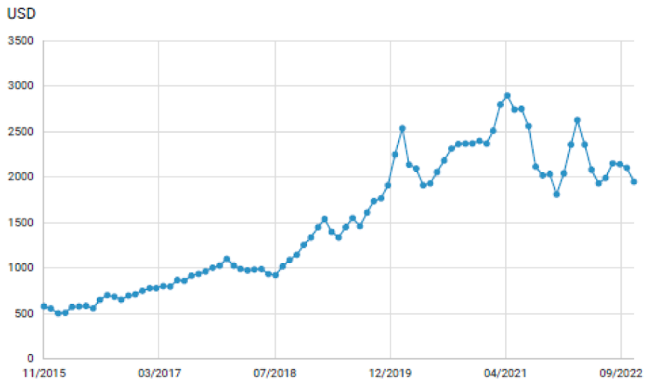

Figure 16. Price (in $) for one troy ounce of palladium during the period 2015−2022 (analysis data for the last two years are not still available in the consulted reports).[97] One troy ounce corresponds to 31.1035 g.

4. OUTLOOK, CHALLENGES AND FUTURE DIRECTIONS

This section includes a description of the unresolved challenges in the synthesis allyl alcohols and suggests innovative pathways for a sustainable synthetic future. The manufacturing of allyl alcohols heavily depends on petrochemical processes, and this is difficult to accept from a sustainable point of view. However, the rapid production growth of chemicals expected for the next decade, which includes allyl alcohols, really hampers any alternative solution based on renewable sources.

To clearly visualize the gap between academic and industrial approaches to allylic alcohol synthesis, Table 1 summarizes how each major synthetic route is currently addressed in both environments, highlighting the main challenges that must be overcome to reconcile sustainability and scalability. Academic research emphasizes mechanistic understanding, selectivity, and proof-of-concept catalyst design, whereas industrial development prioritizes robustness, scalability, and cost efficiency. Bridging both approaches requires transferring catalytic innovations into stable solid systems, replacing critical metals such as Pd, and coupling renewable-energy inputs with continuous-flow operation.

The most studied solution for the synthesis of allyl alcohol **7** from a renewable, biomass-based starting material is the use of glycerol **30** as an oxygenated C_3 molecule, which needs to be partially dehydro−oxygenated to generate the new alkene functionality. In this sense, the chemical industry is working hard during the past decade, and different patented technologies can be found, which include uncatalyzed and catalyzed processes. Regarding the former, the uncatalyzed dehydro−oxygenation reaction with formic acid allows the conversion of a mixture of glycerol up to 80% yield of allyl alcohol **7** after gradually heating the mixture to reach 260 °C.[98] Although uncatalyzed, the process with formic acid can be streamlined in flow.[99] However, catalytic processes are preferred here, and, for instance, the obtention of **7** from **30** using zeolite catalysts has been patented in the gas phase at 250−450 °C in a fixed−bed reactor with continuous flow.[100]

The academic community is aware of this industrial interests and research on the dehydro−oxygenation reaction of glycerol **30** is a topic of interest, but not much developed. The dehydro−oxygenation reaction with a rhenium catalyst has been reported,[101,102] and the reaction is promoted by different rhenium catalysts, including (pentamethyl)cyclopentyl rhenium

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Table 1. Academic vs Industrial Approaches Across the Main Routes to Allylic Alcohols

synthetic route	academic focus	industrial practice	action needed
epoxidation/isomerization	• mechanistic studies on model epoxides	• continuous isomerization of propylene oxide at high-T	• transfer mechanistic insights to stable solid catalysts
	• noble metals (Pd, Au, TiO_2)	• supported oxides (Li_3PO_4-type)	• extend scope to functionalized alkenes
	• batch operation	• high productivity	
hydrogenation	• homogeneous Pd, Ru, Au systems	• heterogeneous Pd catalysts	• develop Ni, Cu, Fe alternatives
	• selectivity and mechanism oriented	• high Pd loading	• validate long-term stability in flow
		• continuous gas-phase	
glycerol route (thermocatalytic)	• zeolites, Mo−V−O_x, Re catalysts	• not commercialized yet	• conduct pilot-scale testing
	• lab-scale fixed-bed studies	• positive LCA outlook if stability improves	• ensure impurity tolerance
	• **TRL 3−4**		• integrate with biodiesel plants
electrocatalytic (CO_2 routes)	• Cu, MoS_2 electrodes	• no industrial deployment	• increase current density and Faradaic efficiency
	• selectivity studies	• high capital and energy costs	• enable continuous operation with renewables
	• low TRL		
photocatalytic	• Au/TiO_2, Cu(I) oxides	• not applied industrially	• design scalable photoreactors
	• visible-light activation	• low photon flux	• develop hybrid photothermal systems
	• mechanistic focus	• catalyst deactivation	
biocatalytic	• multienzyme cascades	• pilot-scale processes	• improve productivity and enzyme lifetime
	• renewable substrates	• mostly for ethanol/butanol	• integrate with chemocatalytic steps
	• mild aqueous conditions	• cost limits	

trioxide,[101] and methyltrioxorhenium (MTO) and rhenium(VI) oxide,[102] at temperatures of 140 °C, achieving selectivities of 90% in the process if an atmosphere of dihydrogen is used.[102] In addition, it is possible to reuse the rhenium catalysts.[84] Iron oxides are also competent catalysts for this reaction, to produce allyl alcohol **7** from glycerol **30** in 40% yield in a fixed−bed reactor at 350 °C and atmospheric pressure, using potassium as an additive.[103] These results agree well with the catalytic systems based on alkaline modified−HZSM5 zeolites and other metal oxides commented above (see Section 2.3),[104] where the acid site promotes the dehydration reaction while the basic site assists in the hydrogen transfer reaction and imparts stability to the catalyst.[105,106] Therefore, this catalytic design can be spotted as a preferred one for the glycerol **30** dehydro−oxygenation reaction.[107,108] Indeed, both catalytic supports, i.e. zeolites (or mesoporous silica) and metal oxides, can be joined in a single catalyst, after incorporating the latter into the former's framework.[109−112] Sacrificial reductants such as ammonia can be co−fed during the process.[113] Following the rationale that Lewis acid and basic sites are required to efficiently effect the deoxy−dehydration reaction of **30**, amphoteric supports such as CeO_2 have been used as a catalyst for this reaction.[114]

Any new industrial technology for the synthesis of allyl alcohols based on glycerol **30** must also consider the rapid transformation of the allyl alcohol into more elaborated products, as it occurs currently with the petrochemical−based processes. However, a higher research effort seems to be needed in this regard. For instance, the in−situ transformation of glycerol **30** into acrylic acid **55** in 80% yield through allyl alcohol **7** has been reported with multimetallic molybdenum−vanadium−wolframium oxide catalysts in flow and with gold on ceria as a catalyst,[115−118] as well as the epoxidation reaction of allyl alcohol **7** to glycidol has been demonstrated to occur with titanium−containing hierarchically porous zeolites.[119]

Beyond the catalytic developments discussed above, it is also important to evaluate the environmental performance of these technologies under a sustainability framework. Table 2 compares the thermocatalytic conversion of glycerol 30 with the conventional petrochemical routes using selected indicators representative of green metrics and life-cycle assessment criteria. This qualitative comparison highlights the main advantages and limitations of each approach in terms of feedstock origin, energy intensity, catalyst criticality, environmental footprint, and technological maturity. Overall, the glycerol route combines renewable carbon origin, Pd-free catalysis, and improved LCA potential, yet remains less mature than the petrochemical benchmark. Its sustainability advantage will depend on catalyst longevity, impurity tolerance, and process electrification to reach competitive productivity at industrial scale.

Table 2. Sustainability Comparison between the Thermocatalytic Glycerol Route and the Petrochemical Baseline

criterion	glycerol thermocatalytic	petrochemical baseline	key remark
feedstock	renewable C_3 (biodiesel byproduct)	fossil (propylene)	glycerol enables circularity
energy demand	medium (250−450 °C)	medium−high (>400 °C)	potential reduction via heat integration
catalyst	Fe, Mo−V−O_X, Re, zeolites, CeO_2	Pd-based (Li_3PO_4/oxides)	glycerol route can be Pd-free
environmental impact (LCA)	lower CO_2 footprint (biogenic carbon)	higher energy and carbon intensity	environmental gains vs lower TRL
circularity& waste	mainly water, benign byproducts	hydrocarbon purge streams	better waste profile for glycerol route
technology readiness (TRL)	4−5 (pilot/lab scale)	9 (industrial)	needs scale-up and durability

The rest of allyl alcohols are generally prepared by the same methodologies that the simplest allyl alcohol **7**, i.e. the epoxide isomerization reaction, the hydrolysis of allyl derivatives or selective hydrogenation reactions. While the latter has already been commented for different elaborated allyl alcohols in Section 2.2, where some solutions to decrease the amount of palladium catalyst and substitute the polluting Lindlar catalysts

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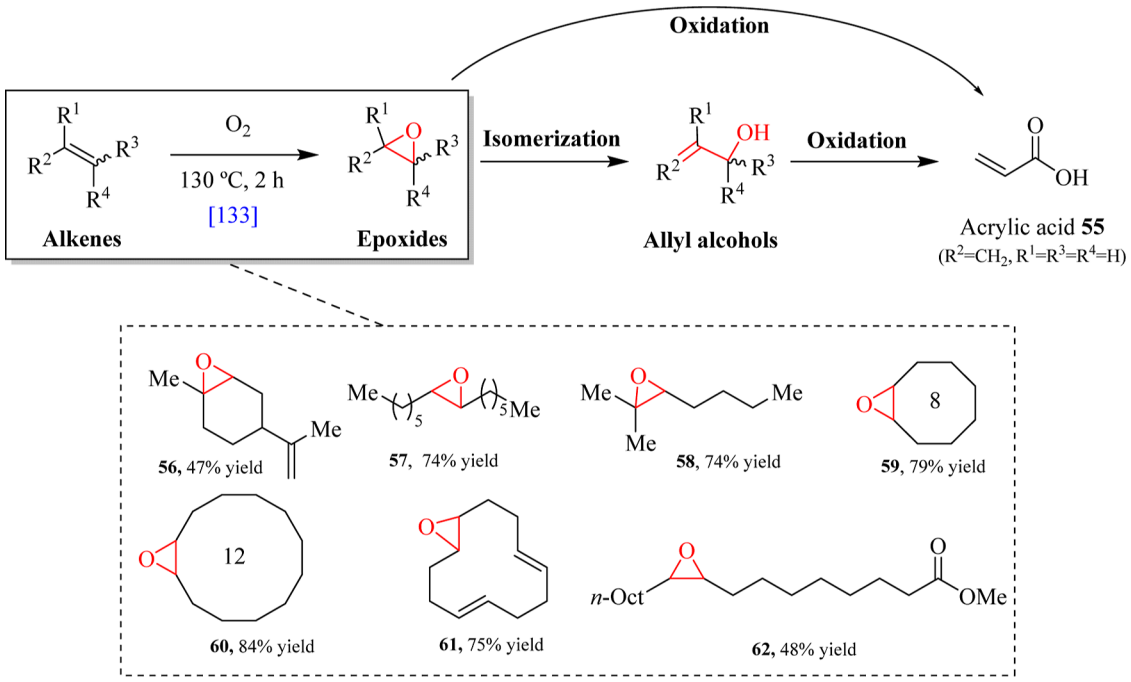

Figure 17. Selected examples (products **56**–**62**) for the aerobic epoxidation of alkenes without any catalyst, additive nor solvent, and potential one–pot reactions, to produce not only allyl alcohols but also highly oxidized products of interest.

have been presented, we will comment here on the need to improve the sustainability of the epoxidation reactions of complex alkenes (beyond propylene **34**). Elaborated alkenes are usually epoxidized with organic peroxidesor,[120] in the more optimal processes, with hydrogen peroxide and a catalyst in solution.[121,122] One representative example is the epoxidation of limonene and other terpenes.[123] Limonene is a multiton waste product of the agrochemical industry and is intensively explored as sustainable source for other more complex organic compounds, particularly limonene epoxide **56**.[124] However, the epoxidation reaction at high scale must not be carried out with typical organic peroxides and the epoxidation of limonene with hydrogen peroxide is not particularly efficient, even with metal catalysts.[125] Therefore, limonene and, by extension, terpene epoxidation reactions, are still not competitive in the market.

In any case, the catalytic system with hydrogen peroxide, while much better than organic peroxides, is arguably still far away of any sustainable modern chemistry and increase significantly the price of the final allyl alcohol. In this regard, molecular oxygen (air) is the ideal epoxidation agent to design a sustainable epoxidation process, which is already in use in the massive production of ethylene oxide, at >500 °C with silver–supported catalysts.[126] Unfortunately, efforts to develop a similar catalyzed epoxidation process with air for other alkenes have not been fruitful, at least for a suitable industrial implementation.[127−132] Our group has very recently reported the epoxidation reaction of complex alkenes with just air, including limonene, without any catalyst, additive nor solvent.[133] Figure 17 shows that this approach could be used to directly prepare allyl alcohols from a variety of epoxides, such as **56**–**62**, all obtained from the corresponding alkenes and air, or even to produce more elaborated oxidized products (i.e., acrylic acid **55**) if the proper catalyst is implemented in–situ. This hypothesis is not unlikely, considered that our work has shown the easy engagement of cascade reactions with the aerobic formation of the epoxide.[133]

As we have previously emphasized, the future of allylic alcohol synthesis will also depend on overcoming the structural dependence on palladium. While several strategies to minimize its use or replace the Lindlar-type catalysts have already been explored, a complete transition toward Pd-free systems remains an open challenge. Promising directions include earth-abundant metal catalysts (Fe, Co, Ni, Cu) capable of driving hydrogenation and deoxydehydration under milder and more sustainable conditions,[103,105] and mixed oxides such as CeO_2 and Mo−V−O_X, which exhibit redox stability suitable for continuous operation.[114−116] Nonmetallic catalytic systems, such as boron- and phosphorus-based frustrated Lewis pairs, offer additional possibilities for H_2 activation without using critical metals. In parallel, biocatalytic and chemo-enzymatic cascades provide complementary low-energy routes that align with circular economy principles. Together, these approaches define a forward-looking framework for Pd-free, sustainable catalysis in the production of allylic alcohols.

5. CONCLUSIONS

The industrial production of allyl alcohols is based on three main synthetic methodologies: the isomerization reaction of epoxides, the hydrolysis of allyl derivatives (for instance chloride and acetate) and the hydrogenation of convenient precursors (for instance acrolein derivatives and propargyl alcohols). In all these approaches, palladium is the metal catalyst of choice, thus a first approach to improve the industrial synthesis of allyl alcohols is to either decrease the amount of the very expensive palladium or employ other more convenient metals. Regarding the use of renewable starting materials, glycerol **30** seems to be the only alternative approach to date, indeed, the search of the term "synthesis of allyl alcohols from renewable sources" in Scifinder does not return any significant result. The annual production of glycerol **30** is at least three times higher than allyl alcohol **7** (3.7

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vs 1.0 megatons) and the price is, inversely, at least four times lower ($0.6 vs $2.2),[111] which encourages the implementation of this synthetic route in industry, even with variants, such as to prepare allyl acetates.[134] A techno−economic analysis supports this assumption.[8] Limonene constitutes a very similar case to glycerol **30**, since the price is relatively cheap for a complex alkene ($10) and the annual production is relatively high (0.05 megatons), thus giving access to complex allyl alcohols at a reasonable cost. Other terpenes can also be employed as starting materials for a more sustainable industrial production of allyl alcohols and, for instance, the terpinolene market price is reasonable ($20, as much as the double than limonene) and it can be employed for the synthesis of terpine−4−ol **10** through terpinolene epoxide **8**. Another very recent example of synthesis of allyl alcohol **7** from renewable sources is the electro electrocatalytic CO_2 reduction, after using a phosphorus-rich copper catalyst operating at a current density of 1100 mA cm^{-2} and with a Faradaic efficiency of 66.9% for C_{3+} products, mainly allyl alcohol **7**.[65] The electrochemical approach, although still in its infancy for the direct synthesis of **7** or any other allyl alcohol by CO_2 reduction and coupling reaction, offers a new alternative solution beyond traditional thermal synthetic processes. In any case, despite these natural sources for allyl alcohol production offer obvious advantages respect to other raw materials in terms of sustainability, this fact does not imply a rapid implementation by the industry since the latter involves significant investments, the construction of new plants or the modification of equipment to achieve the required improvements, besides competing with extremely cheap petrochemical starting materials. A combined effort of industry and academy is necessary here to surmount these difficulties.

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Biographies

Dr Antonio Leyva-Pérez was born and grew up in Seville (Spain). He studied Chemistry at the University of Valencia. After that, he carried out the Ph.D. under the supervision of Prof. Hermenegildo García at Instituto de Tecnología Química (ITQ, UPV-CSIC) and, after a short stay in M.I.T. at Prof. Steven L. Buchwald's laboratories, he did postdoctoral studies at The University of Cambridge in Prof. Steven Ley's group. In 2008, he returned to the ITQ to work with Prof. Avelino Corma and, after receiving a Ramon y Cajal research contract in 2014 and a Distinguished Research position in 2016, he founded the Catalysis for Sustainable Organic Reactions group, and then attained Tenured Scientist (2019) and Researcher Scientist position (2023) at the Spanish Research Council (CSIC). His main interests focus on the frontier between sustainable chemistry, organic synthesis, catalysis, and industrial chemistry.

Dr Marta Mon studied Chemistry at the University of Valencia and did the Ph.D. in the same University under the guidance of Prof. Emilio Pardo Marín and Dr. Jesús Ferrando Soria. During this period, she made two short stays, one in the Laboratoire Structures, Propriétés et Modélisation des Solides (SPMS), Université Paris Saclay, and the other in the Institute of Functional Interfaces (IFG) in Karlsruhe Institute of Technology (KIT). In 2019, she started her postdoctoral period with Dr. Antonio Leyva-Pérez at the ITQ, where she got a "Juan de la Cierva" contract. Her main interests focus on the development of effective homogeneous and heterogeneous catalysts for organic reactions of potential industrial interest.

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