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Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts

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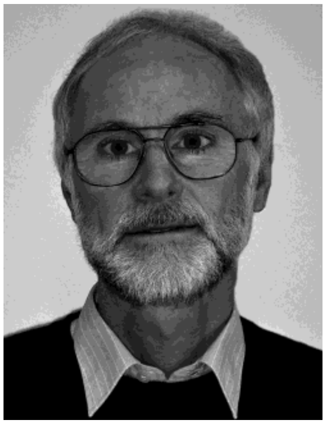
1. Introduction

In the past years there has been a growing demand for solid catalysts efficient in the partial oxidation of alcohols for the production of fine and specialty chemicals. The use of stoichiometric inorganic reagents, though decreasing, is still widespread. The present stringent ecological standards increase the pressure to develop new, environmentally benign methods. In many instances, homogeneous catalysis provides powerful solutions, but on an industrial scale the problems related to corrosion and plating out on the reactor wall, handling, recovery, and reuse of the catalyst represent limitations of these processes.



Tamas Mallat received an M.S. degree in 1972 in chemical engineering and a Ph.D. in 1976 in technical chemistry, both from the Technical University of Budapest, Hungary. He was a postdoctoral associate under G. C. Bond at Brunel University, London, from 1978 to 1979. He continued his academic carrier as a scientist at the Organic Chemical Technology Research Group of the Hungarian Academy of Sciences. In 1990, he moved to the Swiss Federal Institute of Technology (ETH), Zurich, where he is currently a senior scientist. He was awarded a D.Sc. degree in 1994 by the Hungarian Academy of Sciences. His main scientific interest is heterogeneous catalytic oxidation and enantioselective hydrogenation in fine chemistry.

Alfons Baiker (born 1945) studied chemical engineering and received his Ph.D. at ETH Zurich in 1974. Afterward, he spent several years at various universities abroad. In 1980, he completed his habilitation thesis on ammonia synthesis kinetics at Stanford University, California, where he was also involved in teaching courses in kinetics and catalysis. After returning to ETH, he started his own research group, focusing on heterogeneous catalysis and reaction engineering. In 1989 he became associate professor and in 1990 full professor at the ETH. His main research interests are centered around catalyst design, mechanism and kinetics of catalytic surface processes, asymmetric hydrogenation, selective oxidation and environmental catalysis, in situ spectroscopy, and the application of supercritical fluids in catalysis. His goal is to further the scientific basis required for developing environmentally benign chemical processes which make optimal use of raw materials and energy.

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Application of solid catalysts for the gas- or vapor-phase oxidation of simple, small-chain alcohols to the corresponding carbonyl compounds is well established.[1−3] An important requirement is the reasonable volatility and thermal stability of reactant and product—a strong limitation in the synthesis of complex molecules.

Solid catalysts active in the liquid phase under mild conditions have a much broader application range.[4,5] A major challenge in liquid-phase oxidation with solid catalysts is to prevent leaching of the active species.[6] The reactants and particularly the carboxylic acid-type (by)products are frequently excellent chelating agents and accelerate dissolution and deactivation of the catalysts.

The aim of this review is to provide an overview on the various types of materials that have been applied for the heterogeneous catalytic oxidation of alcohols in the liquid phase and extract some general conclusions, where possible. Our intent was not to be all-inclusive; rather we focused on the development in the past 10−15 years. Only those methods will be considered which apply the technically attractive and environment friendly oxidant, molecular oxygen. The numerous catalytic systems using molecular oxygen in combination with additives, such as reducing agents or radical scavengers, are not discussed here due to the environmental impact of the additive or the coproduct formed.

There are different opinions in heterogeneous catalysis whether comparison of the performance of greatly different catalytic materials is fair under identical conditions or under the best conditions identified for each catalyst separately. The former approach is commonly used due to its simplicity. Choosing a different set of conditions, however, can easily reverse the activity or selectivity order, as illustrated schematically in Figure 1. Obviously, a randomly chosen set of reaction conditions cannot provide a suitable basis for catalyst comparison. Here the catalysts are compared on the basis of their best reported performance. We assumed that publications report a good set of parameters and took the best results for comparison that, we hope, are close to the optimum.

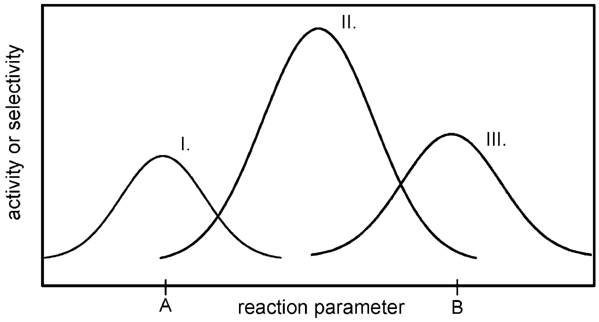


Figure 1. Comparison of catalysts: at conditions A and B the catalysts I and III are the best, respectively, though they are inferior to catalyst II when their performance is compared under the best conditions for each catalyst.

The review is divided into three major sections. The first two include oxidations over intrinsically heterogeneous (solid) and heterogenized metal complex catalysts. The third part compares the best catalysts using some representative and frequently reported test reactions. We hope that this collection will be a valuable reference source to chemists searching for effective solid catalysts and "green" oxidation methods.

2. Intrinsically Solid Catalysts

2.1. Supported Platinum-Group Metals

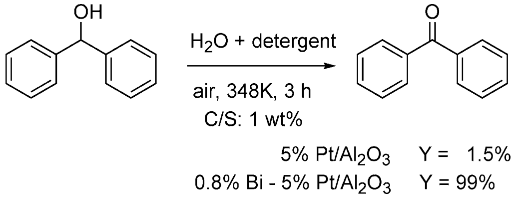
Oxidation of alcohols and polyols over supported noble metal catalysts has been thoroughly investigated in the past years. Details of the early work, in particular the oxidation of carbohydrates and their derivatives (sugar alcohols, aldonic acids, etc.), will not be discussed here. There are numerous books and reviews available on the topic, including the general rules of chemo-, regio-, and stereoselective oxidation of these complex molecules.[7−15]

2.1.1. Catalysts and Reaction Conditions

Pt-group metals can activate alcohols and molecular oxygen under close to ambient conditions and produce the corresponding carbonyl compounds or carboxylic acids in high yields. Today, various bi- and multimetallic catalysts are applied that are more active, more selective, and less prone to deactivation than monometallic catalysts.[11−20]

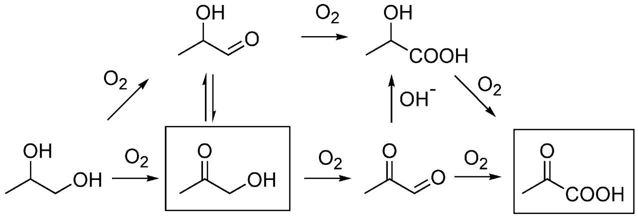
The most commonly used catalysts consist of Pt or Pd as active components and Bi or Pb as promoters, on carbon and alumina supports. Ru and Rh are usually applied without promoters.[21−29] Besides Bi and Pb, a variety of promoter metals have been suggested, including Cd,[30,31] Co,[30,31] Cu,[32] Se,[33] Ce,[33,34] Te,[35] Sn,[36,37] Au,[36,38] and Ru.[36,39] The non-noble metal promoters are inactive under reaction conditions, and their deposition onto the active sites should result in lower oxidation rates. Still, promotion of Pt or Pd may lead to a considerable rate enhancement (Scheme 1)[40−42] and to a remarkable shift in the product distribution (Scheme 2).[32,37,43]

Scheme 1. An Example on the Application of Promoted Pt-Group Metal Catalysts;[41] (Selectivities are 100%)



The bimetallic catalysts can be prepared by simultaneous deposition and reduction of the metal precursors onto a suitable support.[33,44,45] The most commonly used method is, however, the deposition and reduction of promoter onto a supported Pt or Pd catalyst. A variation of this method is the in situ modification; i.e., the promoter metal salt is simply added to the slurry containing the supported Pt-group metal catalyst, and the metal ion is reduced to metal by the alcohol reactant in the early stage of the reaction.[32,46,47] During promoter deposition, metal

Scheme 2. The Best Yields of Hydroxyacetone or Pyruvic Acid Achieved by Promotion of a 5% Pt/Graphite Catalyst in the Oxidation of Propylene Glycol (333 K, water, pH 8)[37]



Pt/C:	37%	44%
Sn-Pt/C:	86%	83%
Pb-Pt/C:	32%	88%

adatoms (submonolayer deposition) and small particles (multilayer deposition) are formed on the surface of the Pt or Pd particles. In addition, particles containing only the promoter metal (M^0 or M^{n+}) may develop on the support, as illustrated in Figure 2. The promoter influences the performance of the neighboring Pt-group metal sites only; thus, the promoter-containing particles on the support are only spectator species. As the non-noble metal promoter alone on the support is unstable in the presence of oxygen and dissolves easily with a suitable anion or chelating agent, this contribution should be minimized.[48] In contrast, metal adatoms on the surface of Pt-group metals are far more resistant against oxidation and dissolution than the corresponding bulk metals.[49−52]

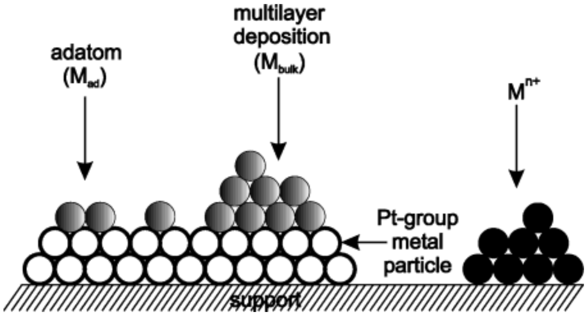
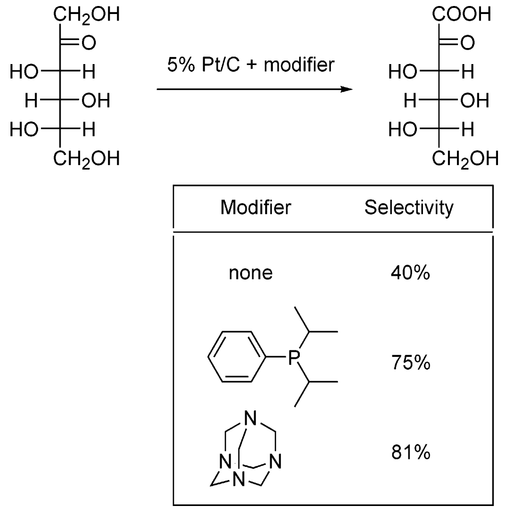


Figure 2. Schematic representation of the structure of a bimetallic catalyst prepared by deposition/reduction of the promoter metal (gray and black) onto a supported Pt-group metal (white) catalyst.

In some cases, good results were achieved with organic compounds as modifiers. These N- and P-containing compounds are simply added to the reaction mixture; they adsorb strongly on the metal surface and improve the rate or selectivity. In the oxidation of L-sorbose to 2-keto-L-gulonic acid, the selectivity of Pt could be doubled by addition of trace amounts of amines[53,54] or phosphines[55,56] (Scheme 3).

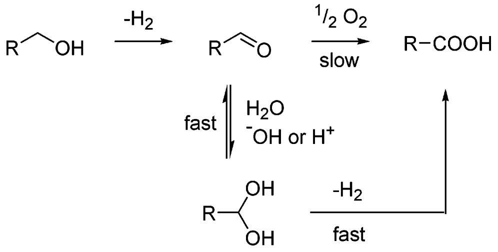
The oxidations are commonly carried out at 330−370 K and ambient pressure or slightly above with air or oxygen. Besides the usual application of a stirred batch (slurry) reactor, there are successful examples of continuous operation.[57−61]

Scheme 3. Oxidation of L-Sorbose to 2-Keto-L-gulonic Acid over Pt Modified by Strongly Adsorbing N- and P-Containing Compounds (323 K, H_2O, pH 7.3, O_2, 1 bar, Selectivity Determined at 50% Conversion)



An advantage of the method is that the catalysts are active and selective in water, though organic solvents,[62−64] ionic liquids,[65] and dense ("supercritical") CO_2 have also been used.[61,66−70] A water−detergent system may be the choice for water-insoluble reactants when flammable organic solvents are to be avoided.[41,43,71] Nonaqueous solvents and relatively high temperature for the rapid removal of the coproduct water are required for the synthesis of aldehydes; these conditions disfavor the hydration of aldehyde to geminal diol and the subsequent rapid dehydrogenation to acid [72−75] (Scheme 4).

Scheme 4. Effect of Water on the Reactivity of the Aldehyde Intermediate on Pt-Group Metal Catalysts



When the target product is a carboxylic acid, precise control of the alkaline pH during reaction is critical to achieve good selectivity, enhance the reaction by facilitating aldehyde hydration and product desorption from the active sites, and avoid metal leaching favored at high pH.[60,76−79] The inorganic base can be replaced by a strongly adsorbing N-base when the reactant or product is unstable in basic medium (Figure 3). This localized basification at the metal surface increases the rate of alcohol dehydrogenation without significantly influencing the pH of the solution.[53]

The C/S mass ratio varies in a broad range; it may be as low as 0.01 for a catalyst containing 1−5 wt % Pt-group metal,[41] but in extreme cases the mass ratio can exceed 1.[80] Similarly, it is difficult to give a characteristic range of reaction rate. The TOF can approach 10 000 h^{-1}, but there are examples showing also values below 1 h^{-1}.[81,82] Besides the role of reactant structure, a probable reason for the big

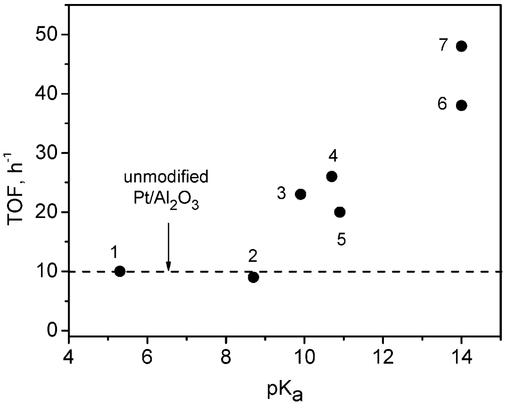


Figure 3. Rate of oxidation of L-sorbose to 2-keto-L-gulonic acid over 5% Pt/Al$_2$O$_3$ modified by strongly adsorbing amines and ammonium hydroxides (323 K, 1 bar, O$_2$, water, modifier/sorbose, 590 ppm). Modifiers: (1) pyridine, (2) diazabicyclooctane, (3) tributylamine, (4) triethylamine, (5) quinuclidine, (6) tetrabutylammonium hydroxide, and (7) tetramethylammonium hydroxide.

variation is the inappropriate choice of catalyst composition. For example, a 1 wt % Pt/C catalyst was completely inactive in the oxidation of phenoxyethanol, but addition of lead and cadmium nitrate promoters to the aqueous solution allowed the fast and almost quantitative transformation to phenoxyacetic acid (TOF = 840 h^{-1}).[46,83]

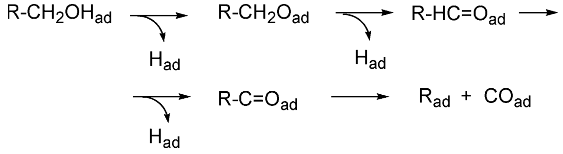
2.1.2. Catalyst Deactivation

A commonly observed deactivation is the "overoxidation" of the active sites.[21,47,73,84−92] It was early discovered that the rate of alcohol oxidation is much higher on a reduced metal surface than on the oxidized surface.[72,93,94] An important consequence of this difference is that the catalyst has to be prereduced before alcohol oxidation by hydrogen or by the reactant itself in an inert atmosphere.[93] Furthermore, the reactor should be operated in the oxygen-transport-limited region; i.e., the rate of oxygen supply should be lower than the actual rate of alcohol dehydrogenation. In the kinetic region, the active sites are successively oxidized and their activity drops. In a batch reactor, the rate of alcohol dehydrogenation decreases with reaction time due to a decrease of alcohol concentration; thus, the rate of oxygen supply has to be adjusted by, e.g., decreasing the oxygen concentration or increasing the temperature toward the end of the reaction. More details on the engineering aspects of alcohol oxidation can be found elsewhere.[19,59,90,95−101]

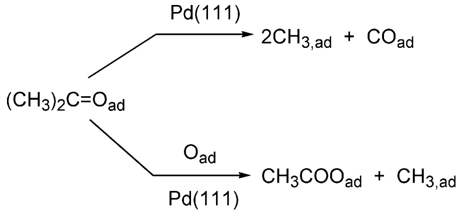
Formation of strongly adsorbed byproducts during alcohol oxidation on Pt-group metals has been frequently reported.[43,80,85,89,102,103] Typical side reactions are the aldol condensation and oligomerization of the carbonyl compound product[104−109] and the decomposition of alcohols mainly via the carbonyl compound formed in situ, affording adsorbed CO and carbonaceous species (C$_x$H$_y$) (Scheme 5).[97,110−125] Even dehydrogenation of the simplest secondary alcohol, 2-propanol, may poison a Pt-group metal already at room temperature (Scheme 6).[126−130]

In contrast to blocking of the active sites by oxygen or byproducts, sintering of metal particles and metal dissolution (leaching) results in irreversible deactivation.[19,42,131,132] Sintering (increase of average metal particle size) at close to ambient temperature is attributed to an atomic migration process, the transport of surface metal atoms "extracted" by chelating molecules (Ostwald ripening).[133] Metal dissolution as M^{n+} species is facilitated by acidic or strongly alkaline pH,[134,135] high catalyst potential (high oxygen coverage), and the presence of complexing agents.[30,76,136,137] In a milder case, the dissolved species redeposit onto larger, thermodynamically more stable metal particles, resulting in particle size enlargement and a loss of active surface area.[48,102,138−140] Metal dissolution can be minimized by applying a low oxygen concentration at the end of the reaction when the alcohol ("reducing agent") concentration is low.[141] Still, leaching remains a limitation in the synthesis of (poly)hydroxy acids, a traditional application of Pt-group metal catalysts.

Scheme 5. Simplified General Route for the Transformation (Decomposition) of a Primary Alcohol on the Pt-Group Metal Surface[110]



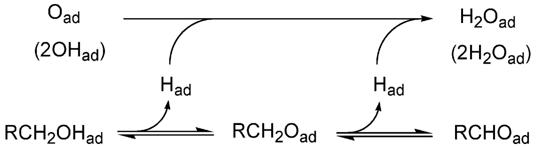
Scheme 6. Simplified Route for the Transformation (Decomposition) of 2-Propanol on a Pd(111) Surface[129]



2.1.3. Reaction Mechanism

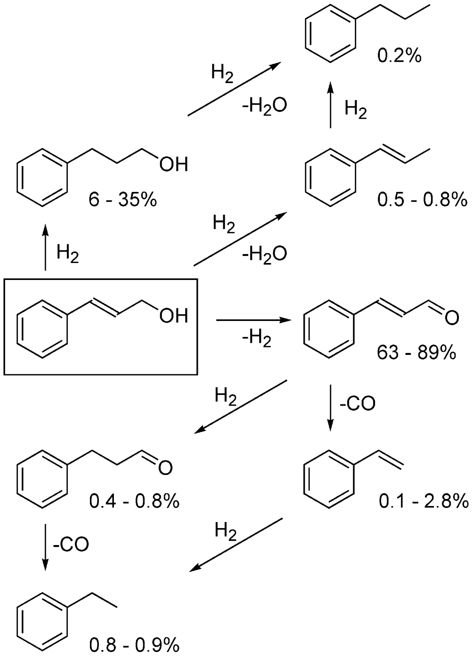
The mechanistic proposals may be divided into three groups. According to the classical dehydrogenation mechanism (model A),[11,13,21,73,142,143] the adsorbed alcohol dehydrogenates in two elementary steps (Scheme 7). The O−H bond of alcohol breaks upon adsorption on the surface sites, affording an adsorbed alkoxide and hydrogen.[144] In the adsorbed alkoxide, the β-C−H bond is weaker than other C−H bonds due to the electron-withdrawing effect of the oxygen atom, leading to the preferential breaking of the β-C−H bond in the rate-determining step.[145] Dehydrogenation is generally catalyzed by bases.[143,146,147] Adsorbed oxygen (or surface OH species in alkaline medium)[148] is necessary to oxidize the

Scheme 7. "Classical" Dehydrogenation Mechanism of Alcohol Oxidation over Pt-Group Metal Catalysts (Model A)



coproduct hydrogen and thus shift the equilibrium toward the carbonyl compound and accelerate the reaction by liberating free surface metallic sites. The inferior role of oxygen in this mechanism is supported by the observations that oxygen can be replaced by a hydrogen acceptor (e.g., an olefin)[149−153] and that the metal catalyst is in a reduced state during oxidation, as demonstrated by electrochemical and EXAFS measurements.[91,95,154−158] A further support for this model is that alcohol oxidation may be accompanied by hydrogenation and hydrogenolysis-type side reactions, displaying a significant H-coverage of the active sites (Scheme 8).[125]

Scheme 8. Reaction Network for the Transformation of *trans*-Cinnamyl Alcohol over 5% Pd/Al_2O_3 (Air, 1 bar, 338 K)



Another class of mechanistic models assumes that the rate-determining step involves direct interaction of the adsorbed oxidizing species with the adsorbed reactant or its partially dehydrogenated intermediate (model B).[16,19,57,159] This interpretation is supported by numerous kinetic studies revealing a Langmuir−Hinshelwood-type behavior,[87,92,103,160,161] and electrochemical[36,41,43,71,92,95,102,162] and X-ray absorption spectroscopic[70] studies that indicate a partial oxygen coverage on the metal surface during some reactions.

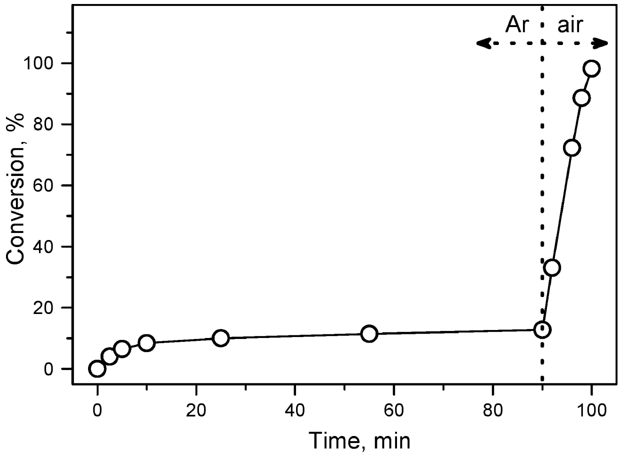


Figure 4. Catalyst deactivation during conversion of cinnamyl alcohol over a 5% Pd/Al_2O_3 catalyst in toluene at 338 K. The initial TOF of 450 h^{-1} in Ar decreased rapidly to 10 h^{-1} due to decarbonylation-type side reactions (see Scheme 8). Introduction of air enhanced the TOF to 2850 h^{-1}. Formation of CO and its oxidative removal by air were confirmed by in situ ATR-IR spectroscopy.

On the basis of recent data, we favor a third approach (model C) adopting the classical dehydrogenation mechanism for the alcohol → carbonyl transformation and presuming that the key role of oxygen is to suppress catalyst deactivation due to strong adsorption of byproducts.[125] According to this model, the oxidative cleaning of the surface sites, or even prevention of the decomposition pathway,[128] is the primary role of oxygen and not the oxidation of the coproduct hydrogen. Partial regeneration of the catalysts by oxidative removal of strongly adsorbed poisoning species can lead to a dramatic rate acceleration compared to anaerobic dehydrogenation (Figure 4),[125] and thus to the (false) conclusion that oxygen is directly involved in the rate-determining step of the reaction. According to this model, some reactions run only on a partially oxygen-covered metal surface because chemisorbed oxygen is necessary to eliminate (oxidize) some surface impurities and liberate active sites for alcohol dehydrogenation.[76,163,164]

Another field of contradictory opinions is the role of metal promoters. Some feasible explanations for the rate and selectivity enhancement are collected below.

(i) Geometric blocking of a fraction of active sites may be responsible for the improved catalyst performance.[36,43,131,134,165] This so-called "ensemble" effect is traced back to the bigger active site ensembles necessary for the formation of poisoning intermediates (by, e.g., C−C bond cleavage), compared to the site requirement of the alcohol dehydrogenation reaction. This interpretation is in line with model C of alcohol oxidation and supported by numerous electrocatalytic studies.[166−168]

(ii) The high regioselectivity in the oxidation of polyfunctional alcohols in the 2-position has been attributed to complex formation between the reactant, a surface Pt or Pd atom, and a neighboring positively charged Bi or Pb promoter (Figure 5a).[11,38,60,79,85,135,169] A similar proposal is the complex formation between a 1,2-diol and a Sn^{IV} species on the Pt surface, resulting in the preferential oxidation of the secondary OH group (Figure 5b).[37] Although

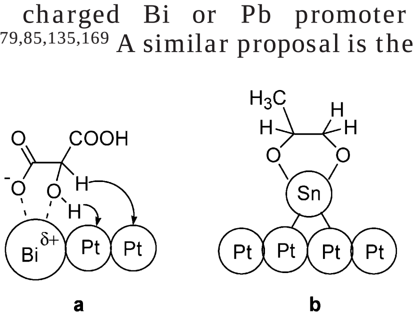


Figure 5. Models assuming complex formation with the substrate as the role of metal promoters in selective oxidations.

the special role of neighboring Pt-group metal−promoter surface sites in the adsorption and dehydrogenation of the reactant is plausible, the (partially) oxidized state of the promoter contrasts to electrocatalytic, LEED, XPS, and EXAFS studies.[52,158,170]

(iii) The rate acceleration and the shift in product distribution may be attributed to bifunctional catalysis, assuming that oxygen or OH radicals adsorbed on the promoter atom are involved in the alcohol oxidation reaction.[36,111,171] This assumption conforms with model B of alcohol oxidation. It may be generalized assuming that the promoter facilitates the oxidative removal of surface impurities, thus supporting model C of alcohol oxidation. Another probable explanation for bifunctional catalysis is that the promoter metal adatoms change the adsorption properties of hydrogen and OH radicals (oxidizing species) due to electronic modification of the surface Pt or Pd atoms.[52,170]

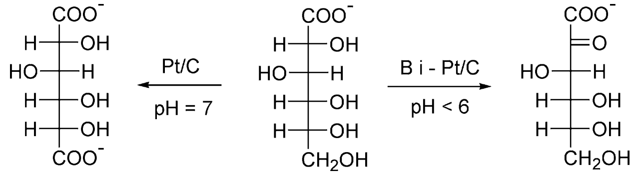
(iv) An ordered alloy (intermetallic compound) formed between the Pt-group metal and Bi, Pb, or Te promoters may be the real active site,[35,80,132,172,173] or the bimetallic site may influence the selectivity,[174] though the observations are contradictory.

(v) It has been shown that the promoting effect of Bi is not due to leaching as Bi^{3+} species.[173,175−178] The presence of a large amount of Bi^{3+} complexes in solution can even inhibit the oxidation reaction, probably due to extensive reduction of Bi^{3+} to (inactive) Bi^0 onto the Pt surface by the reactant alcohol.

2.1.4. Application Range of Pt-Group Metal Catalysts

The application range of supported Pt-group metals, with and without promoters, is very broad. Up to 100% yields have been achieved in the oxidation of various primary alcohols to the corresponding carboxylic acids and of secondary alcohols to ketones. The potential of these catalysts is reflected by the selective oxidation of only one OH function in complex molecules such as aldonic acids (Scheme 9)[38,84,85,136,169,179] and steroidal alcohols.[62,180]

Scheme 9. Selective Aqueous-Phase Oxidation of Sodium Gluconate at 6- or 2-Positions (H_2O, O_2, 333−338 K)[38,169]

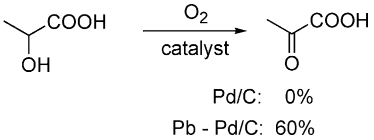


The selective oxidation of an alcoholic OH group has been attained in the presence of the following other functions: alkoxy and aryloxy groups,[83,181,182] phenolic hydroxyl,[183−185] C═C bond (allylic and isolated),[63,186] aromatic aldehyde,[143] amino group,[105] quaternary ammonium group,[187,188] acetamino function,[8] nitro group,[29] nitrile group,[8] aromatic Cl,[32,46,189] trifluoromethyl group,[64] N- and S-containing heteroaromatic ring,[29] and cyclopropyl group.[29] Generally, keto-carbonyl and carboxylic groups are resistant to further oxidation.

An important limitation of these catalysts is the oxidation of aliphatic alcohols to aldehydes.[16] Hydration of aliphatic aldehydes and dehydrogenation of the geminal diol are fast on the Pt-group metal surface, even in nonaqueous solvents (Scheme 4). Rapid removal of the coproduct water by azeotropic distillation improves the yield only moderately.[190] In contrast, hydration of aromatic and α,β-unsaturated aldehydes is minor,[191,192] and their further oxidation by oxygen insertion requires significantly higher catalyst potential than the dehydrogenation step.[43] This is the explanation for the good yields in the synthesis of aromatic, heteroaromatic, and α,β-unsaturated aldehydes, even in aqueous media.

Not only the oxidation of aliphatic alcohols to aldehydes but generally also the synthesis of activated carbonyl compounds is a demanding task due to the poor stability (rapid decarbonylation) of the product. Representative examples for these difficulties and some good solutions are the oxidation of lactic acid to pyruvic acid (Scheme 10),[80,172] L-sorbose to 2-keto-L-gulonic acid (Scheme 3),[56,76,140,193−196] pantoyl lactone to ketopantoyl lactone,[75,197] and α,α,α-trifluoromethyl alcohols to ketones.[64,75]

Scheme 10. Effect of Promoter in the Oxidation of Lactic Acid to Pyruvic Acid (H_2O, pH 8, 363 K)[80]



To sum up, supported Pt-group metal catalysts possess a very broad application range. The technical importance of the method, including the advantage of oxidations in aqueous media, is reflected by the large number of patents. The composition of proven catalysts and the range of practically useful conditions are much extended. A negative aspect of this variety is the demanding optimization process[198,199]—a promising area for combinatorial chemistry.[27,200]

2.2. Supported Gold and Silver

In recent years, the unexpectedly high activity of Au as a low-temperature CO oxidation catalyst[201−204] has initiated intensive research in the use of Au nanoparticles for the liquid-phase oxidation of alcohols. Generally, the adsorption and catalytic properties of Au strongly depend on the particle size, which can be controlled by the preparation method and the catalyst support.[205−213] A crucial and not fully understood question is why small Au nanoparticles exhibit behavior radically different than that of bulk Au.[214−222]

The application range of supported gold in alcohol oxidation is not (yet) broad, and under mild conditions (320−350 K and 1−3 bar oxygen) this oxidation requires a strongly alkaline aqueous medium.[223,224] The aqueous alkaline medium may represent a strong limitation of the method, as various side reactions can diminish the selectivity (keto−enol equilibration, Cannizzaro reaction, oxidative decarbonylation).[205,224] Another drawback is the formation of carboxylates instead of carboxylic acids, though Pt-group metals have the same limitation in the oxidation of primary aliphatic alcohols. In acidic media, gold oxidizes aldehydes to carboxylic acids but is inactive in the transformation of alcohols, and metal leaching may also be significant.[225] An interesting solution is the combination of Au with a Pt-group metal. A 1% Au−0.1% Pd/Al_2O_3 bimetallic catalyst was used for the transformation of 6-hydroxyhexanoic acid to adipic acid.[226] Both the reaction rate and the yield (97%) were high in water, even in the absence of a base, though only at elevated temperature (433 K).

Gold is highly active and selective in the transformation of various diols[205,206,208,218,224,227−230] and glycerol[223,231] to monocarboxylates (Figure 6). Transformation of amino alcohols to amino acids is also selective, but good yields have been reported only for alanine.[228]

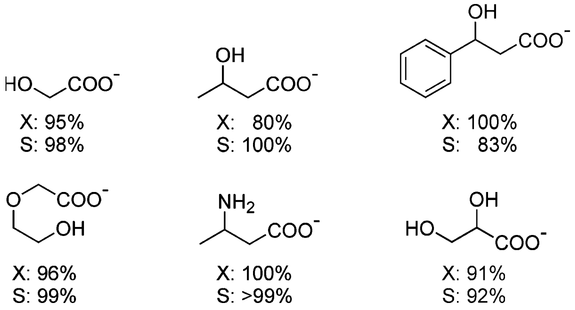


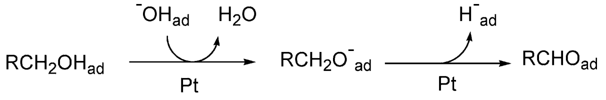
Figure 6. Examples on the synthesis of monocarboxylates from alcohols in aqueous alkaline medium on supported Au nanoparticles.[205,223,228]

The unusually high substrate specificity of supported gold is illustrated by the following comparison. Oxidation of ethylene glycol to glycolic acid was fast (TOF = 1290 h^{-1}), and completion of the reaction required a C/S mass ratio of only 0.03.[230] In contrast, in the transformation of 2-hydroxybenzyl alcohol to salicylaldehyde, the TOF was only around 5 h^{-1}, at an extraordinary C/S mass ratio of over 7.[232,233]

Despite having some similarities to supported Pt-group metals, Au is a distinctly different catalyst. In contrast to Pt-group metals, Au cannot catalyze alcohol dehydrogenation in the absence of a strong base. Further oxidation of aldehydes to carboxylic acids is an oxygen insertion reaction, and this step runs smoothly on Au, even in organic media.[234] In comparative studies of aqueous-phase aerobic oxidation of alcohols with supported Pt, Pd, and Au, the latter was the most selective and the least prone to metal leaching, to over-oxidation by oxygen, and to self-poisoning by strongly adsorbed byproducts.[205,227,231,235] The higher selectivity and absence of catalyst deactivation are probably due to weaker adsorption of oxygen, hydrogen, reactant, and products on Au.[119,123,236]

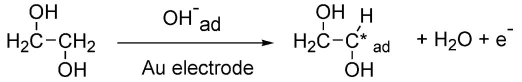
A detailed mechanism of alcohol oxidation on Au nanoparticles has not been reported yet. On the basis of the poor activity of Au in the absence of a base, it was suggested that the rate-limiting step would be H^+ abstraction from a primary OH group of glycerol.[223,231] A similar mechanism was proposed many years ago for alcohol oxidation on Pt/C, involving a second step, the transfer of a hydride ion to the Pt surface (Scheme 11).[8,87,237]

Scheme 11. Alcohol Oxidation on Pt (and Au) Involving Deprotonation of the Alcoholic OH Function by Adsorbed Hydroxyl Ions



We consider it more feasible that the rate-determining step is the cleavage of the C−H bond at the α-carbon atom. A similar mechanism is now generally accepted for Au electrodes (Scheme 12).[238] Despite the structural differences between Au nanoparticles and an extended Au electrode surface, there are also similarities, such as the critical role of aqueous alkaline medium and the absence of deactivation due to decomposition products (CO and C_xH_y fragments).[239,240]

Scheme 12. Rate-Determining Step in the Oxidation of Ethane-1,2-diol on Au Electrode in Aqueous Alkaline Solution



An important question is the nature of active sites on Au nanoparticles. Electrooxidation of ethanol on Au nanoparticles supported on glassy carbon required the partial coverage of Au surface by oxides.[241] Another analogy might be the model proposed for CO oxidation.[219,242,243] According to this suggestion, the active site consists of an ensemble of metallic Au atoms and a cationic Au^+ species with a neighboring OH group (Figure 7).

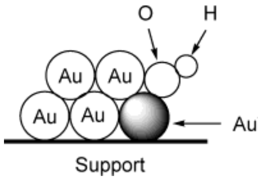


Figure 7. Model of the active site in the oxidation of CO by supported Au nanoparticles.[219]

Silver-based catalysts are well established in the gas-phase oxidation of alcohols and diols[1,3,244−247] but rarely used in the liquid phase. Recently, the quantitative transformation of benzyl alcohol to benzaldehyde in oxygen was achieved over a 0.6% Ag/pumice catalyst under mild conditions (348 K, 1 bar).[248] The material showed reasonably good activity, though the reaction over a similarly prepared 0.27% Pd/pumice catalyst was always faster. The synergic effect observed with Pd−Ag/pumice bimetallic catalysts and with mechanical mixtures of the monometallic catalysts was attributed to cooperation between the Pd^0 and Ag^0 active sites; contribution of the alloy phase detected by EXAFS was excluded.

The inferior performance of carbon-supported Ag, compared to that of various supported Pt-group metal catalysts, has been concluded also in the oxidation of geraniol to citral.[28]

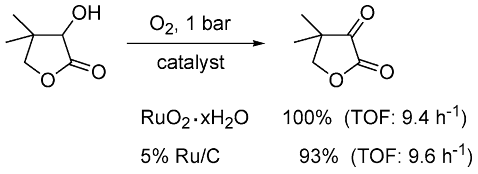
2.3. Oxides and Mixed Oxides

2.3.1. Ru-Containing Oxides

Hydrated ruthenium dioxide ($RuO_2 \cdot xH_2O$) is a stoichiometric oxidant that can be applied also as a reusable catalyst.[249−254] The amount of water (x) is usually in the range 1−1.3 equiv and decreases rapidly with increasing temperature of heat treatment.[255] The material has a two-dimensional structure of independent chains, in which RuO_6 octahedra are connected by pairs of O-bridges. Hydrous ruthenium dioxide is a mixed electron−proton conductor, and the coordinatively unsaturated surface atoms can activate molecular oxygen.[256,257] The oxidation activity of ruthenium dioxide has been attributed to the interaction of strongly bound reactant and weakly bound oxygen species.[258] The completely dehydrated oxide is inactive in alcohol oxidation, and variation in the degree of hydration, which can be controlled by the synthesis procedure, strongly influences the structure and the catalytic activity.[259,260] The hydrous oxide $RuO_2 \cdot xH_2O$ easily transforms into a mixture of Ru and RuO_2 upon thermal treatment at elevated temperature.[253]

Hydrated ruthenium dioxide afforded over 98% yield to cinnamaldehyde in the slow oxidation of cinnamyl alcohol.[261] A drawback of the process is that 2,6-di-*tert*-butyl-*p*-cresol additive was necessary to prevent further oxidation to cinnamic acid. Reactivity of primary and secondary allylic alcohols, α-keto alcohols, α-hydroxy-lactones, and saturated alcohols decreased in this order. Oxidation of pantoyl lactone to ketopantoyl lactone at elevated temperature was quantitative, and the performance of $RuO_2 \cdot xH_2O$ was similar to that of 5% Ru/C (Scheme 13).[197] Obviously, continuous formation of the coproduct water is sufficient to maintain the hydrated state and the oxidation activity of ruthenium dioxide, even at around 450 K.

Scheme 13. Oxidation of Pantoyl Lactone in 1,2-Dichlorobenzene with $RuO_2 \cdot xH_2O$ (at 453 K) and 5% Ru/C (at 446 K)



A novel approach is the synthesis of ruthenium oxide nanoclusters in the supercages of faujasite zeolite (10% RuO_2/FAU).[262] On average, the ruthenium oxide clusters homogeneously distributed in the rigid zeolite framework contained only five Ru atoms, and their size was about 1.3 nm. Strong interactions between RuO_2 chains and framework Si −O functions stabilized the oxide nanoparticles during the hydrothermal synthesis (Figure 8). The recyclable catalyst was active (TOF = 0.5−8.5 h^{-1}) and highly selective (>99%) in the oxidative synthesis of benzaldehyde, cyclohexanone, 2-cyclohexen-1-one, crotonaldehyde, 1-heptanal, and 2-heptanone. In comparative experiments, in the oxidation of benzyl alcohol, 10% RuO_2/FAU afforded 6-fold higher yield to benzaldehyde than bulk $RuO_2 \cdot xH_2O$. This rate enhancement is particularly impressive when considering the probable diffusion limitation inside the zeolite particles. It was demonstrated that the narrow channels of faujasite zeolite around the ruthenium oxide clusters strongly influenced the reactivity of bulky substrates (shape selectivity). In the competing oxidation of benzyl alcohol and 9-hydroxyfluorene, only benzyl alcohol was oxidized, though bulk $RuO_2 \cdot xH_2O$ afforded the facile oxidation of both substrates. These experiments provide additional evidence for the location of ruthenium oxide particles inside the zeolite supercages.

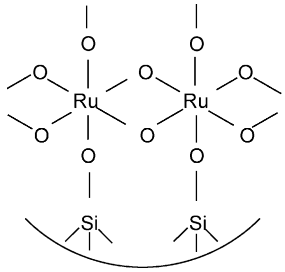


Figure 8. Structure of RuO_2 in the supercages of faujasite zeolite.[262]

Synthesis of mixed oxides by co-precipitation is another approach to tune the catalytic properties of ruthenium oxide. A remarkable synergism was observed in the oxidation of cinnamyl alcohol by addition of Co (Co/Ru atomic ratio 1.5; TOF up to 38 h^{-1}).[254] Primary aliphatic alcohols were less reactive (TOF = 1.3−5 h^{-1}), and further oxidation of aldehydes to carboxylic acids could be suppressed only by addition of a radical scavenger. Cobalt oxide alone was inactive under the same conditions, and the synergic effect of Co was attributed to activation of oxygen in reoxidation of the ruthenium hydride species formed after dehydrogenation of the substrate.

A similar multicomponent catalyst is $Ru_{0.3}Co_2Ce$ oxide.[263] The black powder synthesized by co-precipitation was active (TOF = up to 13 h^{-1}) and highly selective in the oxidation of aromatic and allylic alcohols. Over 99% yields were obtained in various reactions, even in the synthesis of bulky aliphatic and aromatic aldehydes and ketones (e.g., 2-adamantanone, diphenyl ketone, 1-pyrenecarboxaldehyde; TOF = 5−11 h^{-1}). An interesting feature of this three-metal oxide is the oxidation of primary aliphatic alcohols to carboxylic acids, and α,ω-primary diols to lactones, in good yields (Y = 64−97%; TOF = 0.7−2.5 h^{-1}). Addition of a radical scavenger prevented aldehyde oxidation, and aliphatic aldehydes could be prepared in quantitative yields. Oxidation of 1,4-pentanediol (which contains primary and secondary OH functions) afforded methyl γ-butyrolactone in 87% yield.

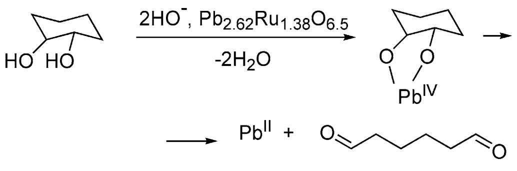
Other effective Ru-based mixed oxides developed for alcohol oxidation include $Ru_{0.35}MnFe_{1.65}O_4$[264] and $Ru_{0.45}MnFe_{1.4}Cu_{0.15}O_x$.[265] The catalysts were designed using ferrite spinel (Fe_2MnO_4) as a model, in which Fe is partially substituted by Ru and Cu. The multicomponent catalysts were prepared by co-precipitation from aqueous solutions. Compositional variations proved that Ru is by far the most active component. The yields with $Ru_{0.35}MnFe_{1.65}O_4$ were excellent in the oxidation of benzylic, heteroaromatic, allylic, and bulky cycloaliphatic alcohols to aldehydes and ketones.[264] In all reactions, including the oxidation of simple aliphatic alcohols such as 1-octanol, the selectivities were at least 99%. The catalyst was reusable without significant loss in activity or selectivity. The TOFs were moderate ($0.2-4.1\ h^{-1}$), and a C/S mass ratio over 1 was used, though the unusually mild reaction conditions (room temperature, air) are probably far from the optimum.

Successful application of conducting lead–ruthenium and bismuth–ruthenium pyrochlore oxides in electrocatalytic reactions[266,267] initiated their synthetic application in alcohol oxidation.[268] The catalysts have an expanded lattice pyrochlore structure with the general composition $A_{2+x}Ru_{2-x}O_{6.5-7}$, where A = Bi or Pb and $0 < x < 1$. Generally, an increasing substitution (x) enhances the catalytic activity.[269] Oxidative stability of Ru–pyrochlore oxides depends on the amount of oxygen vacancies: a large number of oxygen defects decreases the stability.[270] The black macroporous materials function only in strongly alkaline aqueous media.[269,271]

Ruthenium pyrochlore oxides were active under mild conditions in the oxidative cleavage of 1,2-cyclohexanediol.[268,269] Selectivity to adipic acid (70–99%) increased at higher C/S ratios, which was best achieved in a continuous-flow trickle-bed reactor. A limitation of the method is that the catalysts are active in several other oxidation reactions, including the oxidation of ketones, primary alcohols, and olefins. Hence, it is understandable that Ru–pyrochlore oxides were not selective in the oxidative cleavage of carbohydrates and polysaccharides.[272,273]

The probable mechanism of diol cleavage over a Pb–Ru pyrochlore oxide involves a chelated diol intermediate coordinated to a Pb^{IV} site at the catalyst surface (Scheme 14).[274] Reoxidation of the Pb^{II} site is mediated by the neighboring Ru=O lattice site.

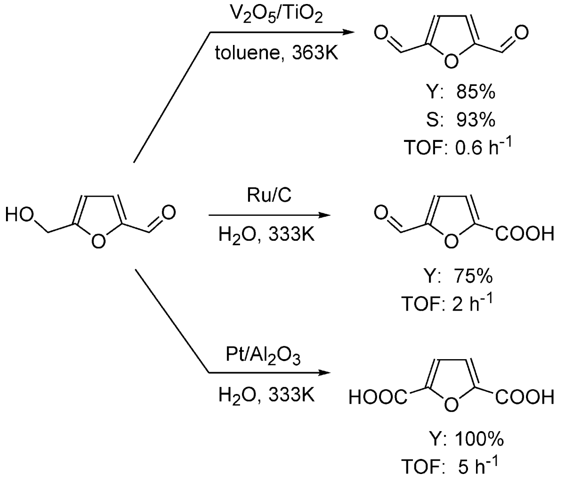
Scheme 14. Oxidative Cleavage of a Vicinal Diol by Ruthenium Pyrochlore Oxide



2.3.2. Other Oxides

Most of the oxides commonly used in gas-phase oxidations are barely active catalysts with molecular oxygen under mild conditions, and reports on their successful applications in the liquid phase are scarce. An example is V_2O_5 supported on TiO_2, a well-known catalyst for gas-phase aerobic oxidation of various substrates.[275–277] The moderately active material afforded good yield in the oxidation of 5-(hydroxymethyl)furfural to 2,5-furandicarboxaldehyde (Scheme 15).[278] The preferred catalyst contained multilayer V_2O_5 on the support, a structure close to that of bulk V_2O_5. For comparison, supported Pt-group metal catalysts produced the formyl–carboxyl or dicarboxyl derivatives in good yields.[22,143]

Scheme 15. Oxidation of 5-Hydroxymethylfurfural with Air over 15% V_2O_5/TiO_2,[278] 5% Ru/C, and 5% Pt/Al_2O_3[22] Catalysts



A broad range of oxides and mixed oxides were tested in the synthesis of ethyl pyruvate from ethyl lactate.[279] Many of them were surprisingly active already at 403 K and converted ethyl lactate at a C/S mass ratio of only 0.0002. No byproducts formed on SnO_2 and ZrO_2 at low conversions, but the selectivity dropped rapidly with increasing conversion, and even the best catalyst, SnO_2-MoO_3, gave only 50% yield.

MnO_2 is commonly used as an oxidizing agent in a large excess, but ultrasonication of the activated oxide ($MnO_2 \cdot xH_2O$) provided a catalytically active material.[280] Diphenylmethanol was transformed to benzophenone with only 0.1 molar equivalent of active manganese dioxide at 363 K in oxygen, but oxidation of cinnamyl alcohol was sluggish, and no reaction occurred with 2-octanol. It was assumed that the surface OH groups were the active sites on the hydrated catalyst.

Hydrous PdO was moderately active and selective in the oxidation of benzyl and cinnamyl alcohols to aldehydes.[281] Synthesis of binary oxides by addition of Co^{3+}, Fe^{3+}, or Mn^{3+} afforded far more efficient hydrated binary oxides ($TOF = 19-25\ h^{-1}$). None of the added components were active alone, in the absence of PdO. A disadvantage of these co-precipitated mixed oxides is the slow oxidation of aldehyde to carboxylic acid, a side reaction that could not be eliminated even by the addition of a radical scavenger, 2,6-di-*tert*-butyl-*p*-cresol. Other important side reactions, the formation of benzene by decarbonylation of benzaldehyde and that of 3-phenyl-1-propanol by transfer hydrogenation of cinnamyl alcohol, indicated that the substrate alcohol presumably reduced PdO to metallic Pd in the binary oxides and the actual catalysts were oxide-supported Pd^0.[281]

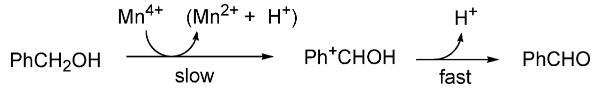
2.4. Molecular Sieves

Various substituted zeolites, also termed “redox molecular sieves”, have been tested in alcohol oxidation in the liquid phase, but most of them require a peroxide as oxidant.[5,282–288] An exception is a Cr-substituted aluminophosphate, CrAlPO-5,[289,290] which catalyzed alcohol oxidation with oxygen in the presence of at least 0.1 equiv of TBHP (*tert*-butyl hydroperoxide). However, a thorough investigation revealed that the real active species was Cr, leached in trace amounts in the presence of oxidant.[6]

Recently, a synthetic cryptomelane-like manganese oxide octahedral molecular sieve, K-OMS-2, was proposed as a selective catalyst that can utilize molecular oxygen.[291] This material, with a composition of $KMn_8O_{16}\cdot nH_2O$, contains one-dimensional tunnels with MnO_6 octahedral building blocks and K^+ as tunnel cation. Relatively simple synthesis methods afford up to 250 $m^2\ g^{-1}$ BET surface area, though the pore size is in the range 0.45−0.7 nm[291,292]—a strong limitation in the transformation of bulky substrates. Oxidation could be accelerated by partial replacement of K^+ by H^+ ions to form Brønsted acidic H-K-OMS-2. The activity of H-K-OMS-2 was, however, still low in the oxidation of various simple aliphatic, cycloaliphatic, aromatic, and allylic alcohols (TOF = 0.035−0.5 h^{-1}).[292−294] Besides the probable mass transport limitation in the narrow pores, the low activity might be due to catalyst poisoning by water, the only coproduct of the reactions. The major advantage of the recyclable catalyst is the excellent selectivity: always 100% to the corresponding aldehydes and ketones.

The large kinetic isotope effect observed in the oxidation of benzyl alcohol implies that removal of hydrogen from the α-C-atom is the rate-controlling step.[293] As concerns the overall process, the reaction obeys the Mars−van Krevelen mechanism[295,296]—one of the few examples of this mechanism in liquid-phase oxidation reactions. Removal of two protons from the organic substrate is accompanied by a two-electron reduction of the Mn^{4+}-type Lewis acidic sites (Scheme 16). The Mn^{2+} sites are reoxidized by molecular oxygen, and facile decomposition of the intermediate H_2O_2 on the molecular sieve produces water, the final coproduct.[293]

Scheme 16. Mechanism of Benzyl Alcohol Oxidation on Manganese Oxide Octahedral Molecular Sieve, K-OMS-2

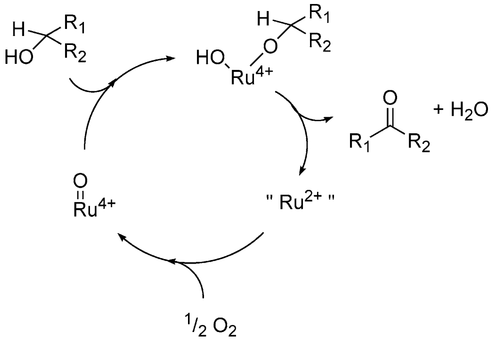


2.5. Hydrotalcites

Hydrotalcites ("HT"), that is, Mg- and Al-hydroxycarbonates with the formula $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$, are relatively new materials in catalysis.[297−301] These anionic clays consist of cationic Brucite layers with anionic compounds in the interlayer. Two- and three-valent cations can be introduced into the Brucite layer, and the anions can also be varied. The general formula of hydrotalcite-like compounds (also termed "layered double hydroxides", LDH) is $[M^{II}M^{III}A\text{-HT} = M^{II}_{1-x}M^{III}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where A is an anion.

A recyclable catalyst, Ru-Mg-Al-HT $\{Ru_{0.5}Mg_6Al_2(OH)_{16}CO_3\}$, showed moderate activity (TOF = 0.3−1.9 h^{-1}) in the oxidation of activated alcohols with molecular oxygen.[302] The C/S mass ratio was rather high, around 1, but the selectivity to carbonyl compounds was usually high, and quantitative transformation of some aromatic alcohols was achieved. Further oxidation of aromatic aldehydes to carboxylic acids was not detected. Primary alcohols were transformed faster than secondary alcohols. The catalyst having 7.3 wt % Ru in the Brucite layer was superior to materials in which other transition metals (Ni, Fe, Mn, V, or Cr cations) were introduced as active species. Variation of the anion in the interlayer of Ru−Mg−Al−HT showed that the catalyst with carbonate ions was the most active. It has been assumed that the active sites are hydroxyl groups associated to Ru cations (Scheme 17).[300,302] In the first step, a basic OH group catalyzes the formation of Ru-alkoxide, and the subsequent β-elimination gives the carbonyl compound. The redox cycle is completed by reoxidation of the reduced Ru species with molecular oxygen.

Scheme 17. Mechanism of Alcohol Oxidation over Ru-Co-Al-HT[300]



Further substitution of Mg ions with Co or Mn ions in Ru-Mg-Al-HT led to a prominent synergic effect.[303] The most active and selective catalyst was Ru-Co-Al-HT, which oxidized a variety of aromatic and aliphatic alcohols to aldehydes and ketones in good to excellent yields (TOF = 0.8−14 h^{-1}). Ru-Co-Al-HT was active also in the oxygenation of aromatic compounds at benzylic positions.[300] For example, fluorene and xanthene were transformed at 343 K to the corresponding ketones in 93−98% yield. The synergic effect between Ru and Co ions was attributed to the formation of higher oxidation state Ru ions.[300,303] Interaction between Ru and Co was evidenced by XPS by a shift in the electronic state of Ru.

A similar catalyst, Ru-Cu-Al-HT, showed low activity (TOF < 1 h^{-1}) with molecular oxygen in the absence of a co-oxidant, such as PhIO or tetrabutylammonium periodate.[304] On the basis of XPS analysis, an interaction was assumed between the two redox couples Cu^0/Cu^{2+} and Ru^{4+}/Ru^{6+} during alcohol oxidation.

There are several hydrotalcite-like materials which were developed for the aerobic oxidation of alcohols and do not contain Ru as the active species. For example, the recyclable catalyst Ni-Al-HT[305] afforded good yields in the transformation of aromatic and allylic alcohols to the corresponding carbonyl compounds, but the reactions were slow, even at a C/S mass ratio above 2. Secondary benzylic alcohols were more reactive than primary alcohols, and substituted benzylic alcohols reacted faster than benzyl alcohol, independent of the electron-withdrawing or electron-releasing character of the function. The catalyst was poorly active in the oxidation of primary and secondary aliphatic alcohols. The catalytically active species is probably Ni in association with aluminum oxide.[305]

Numerous hydrotalcite-like materials containing Co, Cu, Cr, Fe, Mn, Ni, and Zn were tested in the solvent-free oxidation of benzyl alcohol.[306] At the high reaction temperature of 483 K, benzaldehyde formation was only about 5 times faster with the most active catalyst, Cu-Cr-HT, than the uncatalyzed oxidation reaction.

2.6. Phosphates

Hydroxyapatites[307,308] gain increasing interest in catalysis due to their unique properties.[309−311] Hydroxyapatites can be synthesized by various methods, including simple co-precipitation,[308,312−315] and a great variety of new materials can be developed by surface modification[316−318] or by using the ion-exchange ability of apatites.[319−321] A Ru-containing hydroxyapatite (RuHAp), prepared by partial replacement of Ca^{2+} ions with Ru^{3+}, gave high yields in the synthesis of aromatic, hetereoaromatic, α,β-unsaturated, and aliphatic carbonyl compounds.[322] The stable and recyclable catalyst was moderately active; the C/S mass ratio was around 1, despite the high Ru content (17 wt %). Interestingly, at 333 K, RuHAp oxidized 1-octanol to octanal in 94% yield without further oxidation to carboxylic acid, and at 353 K, octanoic acid formed in 82% yield. Primary aliphatic alcohols were preferentially oxidized in the presence of secondary alcohols. This chemoselectivity resembles the properties of $RuCl_2(PPh_3)_3$[323] and contrasts those of "bulk" Ru catalysts (RuO_2, Ru/Al_2O_3), indicating the presence of isolated Ru cations as active species in RuHAp.[322] The active sites are probably monomeric Ru cations surrounded by O and Cl,[322] though no Cl has been found recently in a similar catalyst.[324] Ru is strongly coordinated to the apatite framework, and this interaction prevents leaching of the active species. The structure shown in Figure 9 explains why the authors classified the material as a supported Ru complex.[322] According to their model, the oxidation is initiated by a ligand exchange between the alcohol and the chlorine species at the Ru site. The carbonyl compound product is formed by β-hydride elimination from the Ru−alcoholate. Interestingly, the application range of RuHAp is quite broad: it is active and selective in the aerobic oxidation of primary amines to nitriles[325] and organosilanes to silanols,[326] and in the racemization of chiral alcohols.[324]

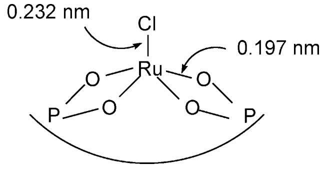


Figure 9. Isolated Ru^{3+} species with the nearest oxygens on the surface of hydroxyapatite, as identified by XANES, XPS, and EDX analysis.

A similar catalyst, Pd−hydroxyapatite, was prepared by interacting stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ with a solution of $PdCl_2(PhCN)_2$.[327] The catalyst containing only 0.3 wt % Pd was far more active than the Ru analogue (TOFs up to 500 h^{-1}) and afforded good yields to various aldehydes and ketones. The unused catalyst contained monomeric $PdCl_2$ species grafted by chemisorption onto the apatite surface (Figure 10). Analysis of the structure of the recovered sample revealed, however, that during reaction Pd^{2+} was reduced to Pd^0 by the reactant alcohol and the actual catalytic species were apatite-supported Pd nanoparticles with an average diameter of 4 nm. Accordingly, this catalyst belongs to the class of supported Pt-group metals discussed in section 2.1.

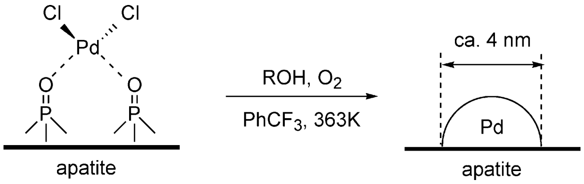


Figure 10. Structure of as-synthesized Pd-exchanged hydroxyapatite (left) and its restructuring to a supported metal catalyst (right) under alcohol oxidation conditions.

Pd^{2+} was resistant against reduction when a nonstoichiometric, Ca-deficient hydroxyapatite, $Ca_9(HPO_4)(PO_4)_5(OH)$, was applied for ion-exchange using the same method as described above. Interestingly, this catalyst was active in Heck and Suzuki reactions but not in alcohol oxidation with molecular oxygen.[327]

Recently, $Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$ have been proposed for the aqueous-phase aerobic oxidation of benzyl alcohol and cyclohexanol.[328] The reaction rates were low, and the highest yield of the corresponding carbonyl compounds was only 12%.

3. Heterogenized Metal Complexes

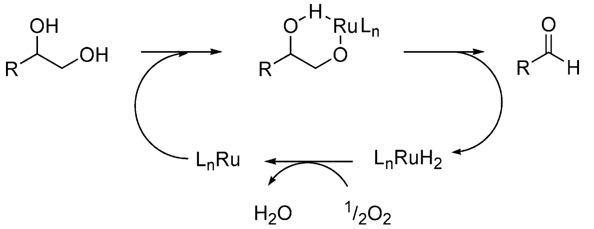
For immobilization of soluble catalysts active with molecular oxygen, various conventional techniques[329−333] have been applied, including incorporation of metal ions into lattices, adsorption on a high surface area support, ion exchange, covalent bonding via tethers, and entrapment into a porous support. As concerns the stability of these hybrid catalysts, simple adsorption on a support can rarely prevent leaching of the active species, and the oxidative stability of polymeric supports is frequently insufficient.

In some cases, new materials are designed and described as supported metal complexes, but the published data reveal that, during preparation, the metal ions were reduced to metal (M^0). For example, a polytitazane−platinum complex on magnesium oxide support was suggested as a supported complex catalyst for alcohol oxidation.[334−337] The black color of the final material and particularly the XPS data indicate, however, that the catalyst likely contained small Pt particles dispersed in the organic−inorganic matrix. Accordingly, these materials belong to supported Pt-group metals (section 2.1) and will not be discussed here.

3.1. Ru-Based Catalysts

A simple method, adsorption on activated carbon, was applied for the heterogenization of $Ru(PPh_3)_3Cl_2$.[338] The support enhanced the reactivity of the complex in the oxidative cleavage of vicinal diols to aldehydes, and fair to good yields at moderate rates (TOF = 1.5−3 h^{-1}) were achieved in hydrophobic solvents. The highest selectivity to aldehydes was measured in the oxidation of terminal diols, though the transformation of internal vicinal diols to aldehydes and cyclic diols to α,ω-dialdehydes was also efficient. A disadvantage of the method is the high C/S mass ratio (up to 4), and it is not known whether the catalyst is truly heterogeneous and recyclable. Formation of a dialkoxyruthenium complex leading to a six-membered transition state was proposed for the reaction mechanism, as illustrated in Scheme 18.

Scheme 18. Cleavage of 1,2-Diols by $Ru(PPh_3)_3Cl_2$/C via a Six-Membered-Ring Transition State[338]



A general deficiency of the adsorption technique is that the metal in its highest oxidation state has the lowest affinity to the support, resulting in considerable leaching of the active species during oxidation.[332] This limitation is illustrated by the oxidation of alcohols with another carbon-supported Ru complex, $[RuCl_2(p\text{-cymene})]_2$.[339] The catalytic properties of the immobilized complex remained similar to those of the homogeneous complex.[340,341] Benzylic and allylic alcohols were oxidized in the presence of 5 mol % base, Cs_2CO_3. Reasonable rates (TOF = 1.6−14 h^{-1}) and good yields of the carbonyl derivatives were achieved, but the C/S mass ratio was well above 1, and more than 30% of the complex leached out of the support during a 9-fold catalyst recycling test.

Polyoxometalates[342−346] are proven catalysts of oxidation and dehydrogenation reactions. They are sufficiently stable, possess high oxidation potential, and are reoxidized by molecular oxygen. An effective heterogeneous oxidation catalyst, Ru-substituted silicotungstate, $[(n\text{-}C_4H_9)_4N]_4H[SiW_{11}Ru(H_2O)O_{39}]\cdot 2H_2O$, was synthesized by the reaction of $RuCl_3$ with the polyoxometalate in an organic solvent.[347] The catalyst was insoluble in various weakly polar organic solvents and could be recycled without any significant loss in activity. A strong synergic effect was observed between the Ru^{3+} active site and the polyoxometalate $[SiW_{11}O_{39}]^{8-}$, allowing fast reaction (TOF = 15−23 h^{-1}) even at low C/S ratios of only a few weight percent. Various aliphatic, cycloaliphatic, and aromatic ketones were prepared in 67−99% yield. Oxidation of primary aliphatic and aromatic alcohols was slower and gave a mixture of aldehyde and carboxylic acid. Oxidation of allylic alcohols barely proceeded. In contrast, the catalyst was active in the oxidation of some alkanes, such as adamantane.

Attaching ligands to an insoluble polymer support is a popular strategy to heterogenize soluble complexes, but it has never worked very well. A recent example is the immobilization of a Ru(III)−Schiff base complex on the surface of a chloromethylated styrene−divinylbenzene cross-linked copolymer via sequential attachment of ethylenediamine, salicylaldehyde, and $RuCl_3$ (Figure 11).[348,349] No byproduct was detected in the oxidation of benzyl alcohol to benzaldehyde, but about 35% of Ru was lost during the leaching test within less than 6 h.

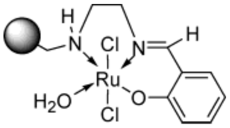
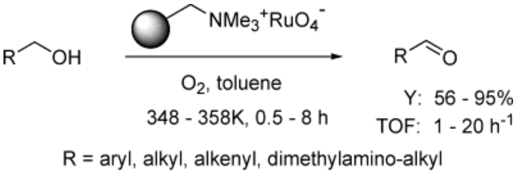


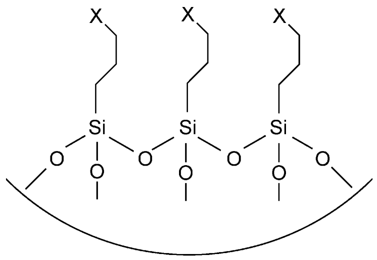
Figure 11. Polymer-anchored Ru(III)−Schiff base complex.[349]

Perruthenate anchored to an Amberlist anion-exchange resin via quaternary ammonium groups was originally developed as a clean oxidant.[350] Later it was shown that it can also be used as a catalyst with oxygen for the transformation of primary alcohols to pure aldehydes (Scheme 19).[351] Nonactivated and secondary alcohols reacted more slowly. Further oxidation of aldehydes to carboxylic acids was not detected, even in the oxidation of aliphatic alcohols. Oxidation of tertiary amino alcohols and epoxyalcohols to aldehydes gave 90−95% yields. In the fastest reaction, in the oxidation of benzyl alcohol, a TOF of 20 h^{-1} was achieved, though at a C/S mass ratio of over 9—a value characteristic of stoichiometric oxidants rather than catalysts. A further limitation to practical application is the difficulty of catalyst recycling, likely due to oxidative degradation of the polymeric support.[352]

Scheme 19. Oxidation of Alcohols by a Perruthenate Supported on a Polymer (Amberlist Anion-Exchange Resin)[351]



In a sophisticated approach, perruthenate was immobilized as a tethered complex on a more stable inorganic material, mesoporous silicalite MCM-41 (Figure 12).[352] The catalyst was recyclable without any detectable metal leaching or decline in the catalytic performance. Various aromatic and allylic alcohols were oxidized quantitatively to aldehydes at



X = $H_3N^+RuO_4^-$, $Me_3N^+RuO_4^-$,
or $Et_3N^+RuO_4^-$

Figure 12. Perruthenate immobilized on a mesoporous silicalite MCM-41.

353 K, at a C/S mass ratio of only 0.1. The presence of C=C bonds and Cl, MeO, BnO, NO_2, CF_3, or F functions in the aromatic ring did not disturb the reactions. Secondary aliphatic alcohols and alkenols, such as cyclohexanol and cyclohexenol, did not react. Though the application range is not broad, this is the most active heterogenized homogeneous catalyst for the oxidation of alcohols with molecular oxygen, affording TOF values up to 170 h^{-1}. Even distribution of the active species on the support surface and the absence of mass transport limitation in the mesoporous structure of MCM-41[286] seem to be critical to the good performance.

A versatile route to prepare solid catalysts is entrapment of a soluble transition-metal complex into organically modified sol−gel silica (“ORMOSIL”).[353,354] The key structural properties of doped sol−gel materials, e.g., hydrophilic−hydrophobic character and pore size distribution, can be tailored according to the requirement of the reaction. A general limitation of the method is that wide pores cannot prevent leaching of the active species, while too narrow pores hamper the diffusion of bulky substrates to the active sites. Recently, tetra-*n*-propylammonium perruthenate (TPAP) was embedded into methyl-modified hydrophobic silica, using methyltrimethoxysilane as a sol−gel precursor.[355] The leach-proof catalyst possessed high surface area and a narrow pore size distribution of around 1.2 nm. Transformation of alcohols to carbonyl compounds was fast only in the case of benzyl alcohol (TOFs in the range 1−13 h^{-1}).

3.2. Pd-Based Catalysts

There is an increasing interest in the synthesis and catalytic application of (heterogenized) ligand-stabilized giant clusters that may be considered as models of supported metal catalysts, or as a link between homogeneous and heterogeneous catalysis.[356−361] The giant Pd clusters dissolve in common solvents and act as homogeneous catalysts,[362] though they can be immobilized on a support to produce a heterogeneous, easily recyclable catalyst.

In the first application to heterogeneously catalyzed oxidation of alcohols with molecular oxygen, a five-shell Pd cluster, $Pd_{561}phen_{60}(OAc)_{180}$ (phen = 1,10-phenantroline), was immobilized on TiO_2 while preserving the original structure and size (ca. 3 nm) of the precursor.[363,364] The cluster contained Pd^0 atoms in the inner part and cationic species (Pd^+ and Pd^{2+}) on the surface, stabilized by phen ligands and OAc anions. The catalyst was reusable, with some loss in yield and selectivity. Various primary allylic alcohols were oxidized in AcOH to α,β-unsaturated aldehydes in up to 99% yield, at good rates (TOF = 0.3−15 h^{-1}). The reactions were slower in benzene, but esterification of geraniol could be eliminated.

The reaction mechanism is assumed to be dehydrogenation of the allylic alcohol coordinated to a cationic Pd species, followed by oxidation of the surface hydride with oxygen to form water. The supported cluster showed low activity for the oxidation of secondary allylic and benzylic alcohols, which was attributed to steric crowdedness around the Pd cations. Isomerization and hydrogenation of the substrate on reduced surface sites were also observed. A hydrogen treatment in acetonitrile removed the phen ligands from the surface of $Pd_{561}phen_{60}(OAc)_{180}/TiO_2$ and decreased the reactivity of the catalyst by a factor of 5.[364] Clearly, the phen ligands play an important yet unknown role in the oxidation process.

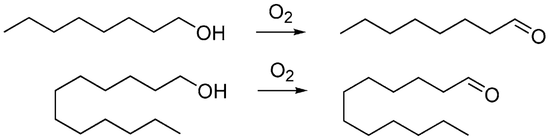
Treatment of $Pd_4phen_2(CO)_2(OAc)_4$ with $Cu(NO_3)_2$ in the presence of oxygen gave a monodispersed eight-shell nanocluster with the approximate composition of $Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$ and an average size of 3.8 nm.[365] The material, immobilized on TiO_2, afforded high yields in the oxidation of primary aromatic allylic alcohols (TOF up to 20 h^{-1}) and benzylic alcohols (TOF = 3 h^{-1}) to the corresponding aldehydes. Electron-withdrawing groups retarded the reaction, and oxidation of saturated alcohols (1- and 2-octanol) barely occurred. A comparison of $Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$ and $Pd_{561}phen_{60}(OAc)_{180}$ nanoclusters revealed significant differences in their reactivity toward allylic and benzylic alcohols.[365]

A palladium−pyridine complex, $\{Pd(OAc)_2(py)_2\}$, was immobilized on the external surface of hydrotalcite by a simple adsorption step.[366−369] The hydrotalcite-supported Pd(II) catalyst was active in a broad range of alcohol oxidation reactions (TOF up to 10 h^{-1}) and gave good yields to aldehydes and ketones. The catalyst was, however, rather unstable, and Pd^{2+} was easily reduced to Pd^0 particles when the alcohol concentration (reducing agent) or the reaction temperature exceeded a certain limit.[369] Besides, the oxidation was sluggish and incomplete without addition of at least 4 equiv of pyridine to Pd(II). Apparently, this heterogenization method was not fully successful.

3.3. V- and Mo-Containing Catalysts (Heteropolyoxometalates)

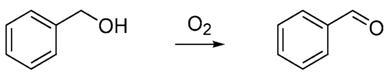
The importance of polyoxometalates and heteropolyacids in catalytic oxidation reactions[342−346] has been briefly discussed in a previous section in connection with Ru-based catalysts. The presence of Ru is not a requirement for oxidation activity. A heterogenized, stable, and reusable catalyst was prepared by impregnation of a mixed-addenda heteropolyanion salt onto activated carbon (10 wt % $Na_5PMo_2V_2O_{40}/C$).[346]

Table 1. Oxidation of Aliphatic Alcohols to Aldehydes



substrate	catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
1-octanol	5%Pt−1%Bi/Al_2O_3	333	$PhCH_3$	142	76	85	189
1-octanol	$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	0.2	51	100	264
1-octanol	Ru^{3+}−hydroxyapatite	333	$PhCH_3$	0.4	94	99	322
1-octanol	$Pr_4N^+RuO_4^-$/ormosil(SiO_2)	348	$PhCH_3$	1	70	100	355
1-octanol	RuO_4^-/polymer	358	$PhCH_3$	1.1	91	100	351
1-dodecanol	Pt	333	C_7H_{16}	13	77	−	146
1-dodecanol	$RuCo_{1.5}O_x$	383	$PhCH_3$	1.3	50	93	254

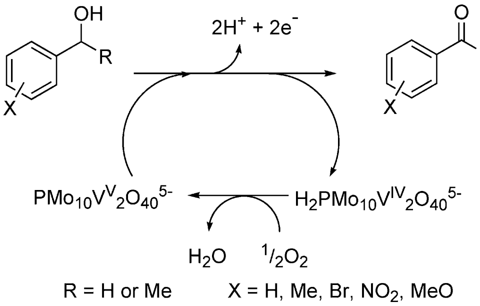
Table 2. Oxidation of Benzyl Alcohol to Benzaldehyde



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
0.5% Pd/Al_2O_3	353	$scCO_2$	1585	87	95	371
0.3% Pd/hydroxyapatite	363	$PhCF_3$	500	99	−	327
1.4% Ru/Al_2O_3	356	$PhCF_3$	40	>98	>99	29
RuO_2·$x$$H_2O$	353	$PhCH_3$	1.4	16	100	262
10% RuO_2/FAU zeolite	353	$PhCH_3$	8.5	>99	>99	262
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	3.4	95	100	264
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	10	>99	>99	263
H-K-OMS-2	383	$PhCH_3$	0.5	97	100	292
Ru-Mg-Al-hydrotalcite	333	$PhCH_3$	1.1	95	97	302
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	9.3	96	96	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	2	>99	>99	322
[$RuCl_2$(p-cymene)]$_2$/C	383	$PhCH_3$	4.7	92	−	339
RuO_4^-/polymer	348	$PhCH_3$	20	>95	100	351
$NR_3^+RuO_4^-$/MCM-41	353	$PhCH_3$	170	100	100	352
$Pr_4N^+RuO_4^-$/ormosil(SiO_2)	348	$PhCH_3$	13	100	100	355
$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}/TiO_2$	333	AcOH	3	92	97	365
$Na_5PMo_{10}V_2O_{40}$/C	373	$PhCH_3$	4.5	97	100	346

Some aromatic primary and secondary alcohols were selectively oxidized to carbonyl compounds in 93−98% yield in toluene without further oxidation to acids (Scheme 20). It was assumed that reoxidation of the catalyst and not the dehydrogenation step was rate-limiting. Aromatic alcohols with electron-donating or -withdrawing substituents reacted at similar rates (TOF = 4.5 h^{-1}), except hydroxybenzyl alcohols (no yield). Oxidation of aliphatic secondary alcohols was slow and incomplete, and primary alcohols were inert. Only 1 mol % of the immobilized catalyst relative to the substrate was used. This ratio, however, corresponds to a C/S mass ratio over 1 due to the low molar concentration of the active species in the catalyst. The catalysts were active also in the dehydrogenation of benzylic amines to aldehydes and ketones in two steps via the Schiff base intermediate.

Scheme 20. Generalized Scheme for Alcohol Oxidation with Carbon-Supported $Na_5PMo_{10}V_2O_{40}$[346]



The same strategy, grafting an ammonium molybdovanadophosphate onto carbon, provided an effective and truly heterogeneous catalyst, $(NH_4)_5H_6PV_8Mo_4O_{40}$/C.[370] The catalyst gave 46−92% yields in the oxidation of allylic and benzylic alcohols to carbonyl compounds under conditions similar to those described above.[346] Interestingly, in a control reaction the unsupported heteropolyoxometalate was inactive (Scheme 21). Limitations to the application of this catalyst as a selective alcohol oxidation catalyst are the necessary high C/S mass ratio (up to 3) and the good activity of the material in the oxidation of amines, alkyl-substituted phenols, and alkanes.[370]

Scheme 21. Effect of Carbon Support on the Oxidation Activity of $(NH_4)_5H_6PV_8Mo_4O_{40}$[370]

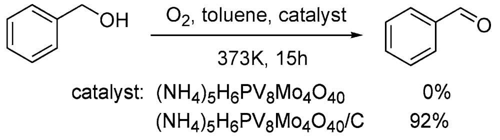
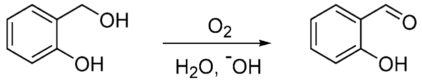
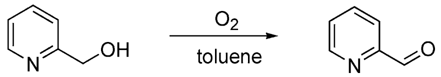


Table 3. Oxidation of 2-Hydroxybenzyl Alcohol to Salicylaldehyde



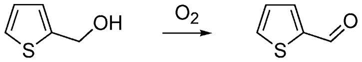
catalyst	T, K	TOF, h^{-1}	Y, %	ref
2% Pt−3.6% Bi/C	318	8500	97	372
1% Pt/C + $Pb(OAc)_2$	303	9440	90	81

Table 4. Oxidation of 2-(Hydroxymethyl)pyridine



catalyst	T, K	TOF, h^{-1}	Y, %	S, %	ref
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	0.4	84	99	264
Ru-Mg-Al-hydrotalcite	333	0.3	50	76	302
Ru-Co-Al-hydrotalcite	333	1.3	91	92	303
Ru^{3+}−hydroxyapatite	353	0.6	>99	>99	322

Table 5. Oxidation of 2-(Hydroxymethyl)thiophene



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
1.4% Ru/Al_2O_3	356	$PhCF_3$	27	>98	>99	29
0.3% Pd/hydroxyapatite	363	$PhCF_3$	6.9	99	−	327
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	13	>99	>99	263
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	3.1	97	99	264
H-K-OMS-2	383	$PhCH_3$	0.5	100	100	292
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	14	91	91	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	3	94	94	322

4. Oxidation of Alcohols on Various Catalysts: A Comparison

It is sometimes difficult to judge the catalytic performance of a new material. One way is to compare the various catalytic materials to the state-of-the-art catalysts in some frequently used test reactions. The comparison based on the data in Tables 1−16 should be considered only as semiquantitative, since in many cases the reaction conditions applied are obviously far from the optimum.

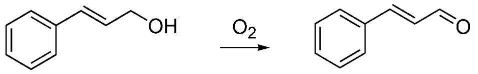
4.1. Primary Alcohols to Aldehydes

Selective oxidation of aliphatic alcohols to aldehydes with molecular oxygen is presumably the most demanding transformation. The majority of known catalysts are poorly active or possesses low selectivity in these reactions, and detailed results are rarely reported. In the oxidation of 1-octanol and 1-dodecanol (Table 1), Pt and particularly a Pt/Al_2O_3 promoted by Bi are by far the most active materials, though they are not very selective. Even the moderate yield of 76−77% to an aliphatic aldehyde is not typical for Pt-group metals, since these catalysts are highly active in the dehydrogenation of the hydrated aldehyde and usually produce the carboxylic acid in high yield (Scheme 4).[68] When high selectivity to aldehyde is critical, various Ru-containing catalysts offer a better choice.

Primary aromatic (benzylic) alcohols can be readily transformed to aldehydes that are relatively resistant to further oxidation, at least under mild conditions. For example, oxidation of benzyl alcohol, the most commonly reported test reaction, is characterized by excellent selectivities and yields on almost all catalysts (Table 2). Outstanding catalysts are Pd/Al_2O_3, Pd/hydroxyapatite, and perruthenate supported on mesoporous silicate MCM-41. Perruthenate is particularly attractive when further oxidation to benzoic acid has to be avoided, though synthesis of the catalyst via tethering is demanding.

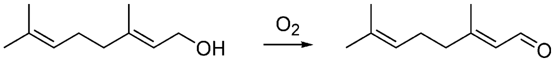
Transformation of 2-hydroxybenzyl alcohol to salicylaldehyde is of practical importance, and this reaction is the fastest among all alcohol oxidation reactions over solid catalysts (Table 3). The catalysts and reaction conditions are discussed mainly in the patent literature. The best TOFs are close to 10 000 h^{-1} over Pt/C promoted by Bi or Pb; the promotion is carried out by simple addition of the promoter metal salt to the reaction mixture. Supported gold nano-

Table 6. Oxidation of Cinnamyl Alcohol to Cinnamaldehyde



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
5% Pt−0.8% Bi/Al_2O_3	313	H_2O + detergent	144	94	>98	43
0.3% Pd/hydroxyapatite	363	$PhCF_3$	72	87	−	327
1.4% Ru/Al_2O_3	356	$PhCF_3$	27	98	98	29
Rh	343	2-PrOH	10	80	96	23
$RuO_2{\cdot}xH_2O$	383	$PhCH_3$	5	79	79	254
$RuCo_{1.5}O_x$	383	$PhCH_3$	38	90	94	254
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	3.9	95	100	264
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	10	>99	>99	263
H-K-OMS-2	383	$PhCH_3$	0.5	95	100	292
Ru-Mg-Al-hydrotalcite	333	$PhCH_3$	1.1	95	97	302
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	14	94	94	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	5.9	99	99	322
$[RuCl_2(p\text{-cymene})]_2/C$	383	$PhCH_3$	2	80	−	339
RuO_4^-/polymer	348	$PhCH_3$	10	>95	100	351
$Pr_4N^+RuO_4^-$/ormosil(SiO_2)	348	$PhCH_3$	1.8	90	100	355
$Pd_{561}phen_{60}(OAc)_{180}/TiO_2$	333	AcOH	15	99	99	363
$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}/TiO_2$	333	AcOH	19	91	98	365

Table 7. Oxidation of Geraniol to Citral



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
5% Pt−1% Bi/Al_2O_3	333	$PhCH_3$	13	>99	>99	189
1.4% Ru/Al_2O_3	356	$PhCF_3$	6	86	97	29
Rh	343	2-PrOH	10	71	85	23
H-K-OMS-2	383	$PhCH_3$	0.5	95	100	292
Ru-Mg-Al-hydrotalcite	333	$PhCH_3$	0.5	100	100	302
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	0.8	71	80	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	2	85	94	322
$Pd_{561}phen_{60}(OAc)_{180}/TiO_2$	333	PhH	0.4	70	100	363

particles also perform well, though the average TOF could not be calculated.[233]

More demanding test reactions are the partial oxidation of the heteroaromatic alcohols 2-(hydroxymethyl)pyridine (Table 4) and 2-(hydroxymethyl)thiophene (Table 5). The yields are high, but the activity of the catalysts is usually low. Most catalysts contain ionic or metallic Ru as the active species. The good performance of Ru/Al_2O_3 and Pd/hydroxyapatite in the synthesis of 2-formylthiophene is surprising in the light of the well-known poisoning effect of sulfur compounds on Pt-group metals.[373−375] A comparison of the data in Tables 2−5 shows that relatively small structural changes can lead to dramatically different catalyst performance. Hence, assessment of the catalysts on the basis of these simple test reactions may be misleading.

Synthesis of α,β-unsaturated aldehydes from the corresponding alcohols is a facile reaction with most solid catalysts, similar to the oxidation of primary benzylic alcohols. Many catalysts give high yields at a reasonable rate in the oxidation of, for example, cinnamyl alcohol (Table 6) and geraniol (Table 7). In both reactions, the most active catalysts are supported Pt-group metals. Among the nonmetallic catalysts, Ru−Co mixed oxide is a good choice, though some other Ru-based catalysts give higher selectivity to the α,β-unsaturated aldehyde. Oxidation of geraniol to *trans*-citral (and of nerol to *cis*-citral) is usually highly stereoselective (E/Z or Z/E > 95/5, respectively),[23,263,264] though the values are not always mentioned.

4.2. Primary Alcohols to Acids

There are very few test reactions commonly used to compare different types of catalysts in the alcohol → carboxylic acid transformation. Additionally, further oxidation of aldehydes to acids is frequently considered as an undesired side reaction, and the catalysts and conditions are optimized in order to avoid this transformation. Table 8 compares some catalysts in the oxidation of 1-octanol and 2-phenoxyethanol. The Ru-based mixed oxide is not very active but affords the free carboxylic acid in high yield without byproduct formation in the nonaqueous medium. Pt-group metals are active and selective, though only in aqueous alkaline media; in the absence of base, oxidation of the aldehyde intermediate is slow and the active sites are partially blocked by the strongly adsorbing carboxylic acid.

Promoted Pt-group metals are the most commonly used catalysts for the oxidative synthesis of carboxylic acids (as salts), including the oxidation of a broad range of functionalized alcohols[32,46,63,83,376] and polyhydroxy compounds.[11−15] A recent industrially important example is the oxidation of a choline salt or hydroxide over 5 wt % Pd/C to give 90% yield to betaine:[187,188,377]

$$[Me_3N^+CH_2CH_2OH]OH^- + O_2 \rightarrow Me_3N^+CH_2COO^- + 2H_2O \quad (1)$$

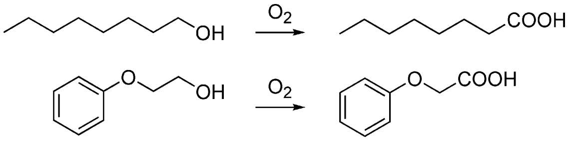
The selectivity of supported Au is also excellent in the oxidation of amino alcohols to amino acids.[228]

4.3. Secondary Alcohols

Oxidation of secondary alcohols to ketones is highly selective, and quantitative transformation without any byproduct formation under mild conditions is not unusual. Representative test reactions for aliphatic and cycloaliphatic alcohols are the oxidations of 2-octanol (Table 9), cyclohexanol (Table 10), cyclopentanol (Table 11), and 2-adamantanol (Table 12). Ru/Al_2O_3 seems to be the most active catalyst (Table 9, TOF = 300 h^{-1}), though the outstanding activity might be due to the elevated reaction temperature and solvent-free conditions. Other Ru-containing catalysts (e.g., Ru−silicotungstate) and supported Pt and Pd also perform well.

The oxidation of secondary aromatic alcohols is illustrated by the transformations of 1-phenylethanol (Table 13) and diphenylmethanol (Table 14). The activity of supported Pt-group metals is remarkably higher than those of other catalysts; the yields are excellent with all catalysts.[29,41,327]

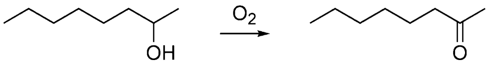
Table 8. Oxidation of Aliphatic Alcohols to Carboxylic Acids



substrate	catalyst	T, K	solvent[a]	TOF, h^{-1}	Y, %	S, %	ref
1-octanol	5% Pt−1% Bi/Al_2O_3	333	H_2O	29	93	97	189
1-octanol	Pd/resin	373	H_2O	0.1	90	−	82
1-octanol	$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	2.5	97	97	263
2-phenoxyethanol	1% Pt/C + $Cd(OAc)_2$ + $Pb(OAc)_2$	343	H_2O	840	98	−	46
2-phenoxyethanol	10% Pd/C + $Bi(NO_3)_3$	343	H_2O	82	100	100	46

[a] Water is used together with some base, and the product is the carboxylic acid salt.

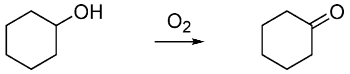
Table 9. Oxidation of 2-Octanol



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
1.4% Ru/Al_2O_3	423	none	300	95	−	29
1.4% Ru/Al_2O_3	356	$PhCF_3$	18	91	>99	29
5% Pt−1% Bi/Al_2O_3	328	H_2O + detergent	78	78	100	*a*
0.3% Pd/hydroxyapatite	363	$PhCF_3$	6.3	91	−	327
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	1	84	100	264
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	6.5	98	100	263
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	4.6	97	97	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	1	96	100	322
Ru−silicotungstate	383	$^{i}BuOAc$	13	79	88	347

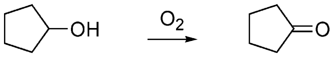
[a] Cs. Keresszegi, T. Mallat, and A. Baiker, unpublished data (C/S, 10 wt %; 1 bar O_2; 3 h; detergent, sodium dodecylbenzene sulfonate).

Table 10. Oxidation of Cyclohexanol



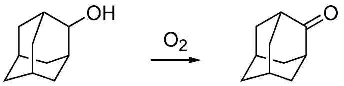
catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
10% Pt/MgO	373	H_2O (pH 9)	7	70	100	378
10% RuO_2/FAU zeolite	353	$PhCH_3$	1.4	43	>99	262
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	0.3	71	100	264
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	1	81	98	263
Ru−silicotungstate	373	$^{i}BuOAc$	23	54	81	347

Table 11. Oxidation of Cyclopentanol



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
10% Pt/MgO	373	H_2O (pH 9)	9.1	100	100	378
1.4% Ru/Al_2O_3	356	$PhCF_3$	4.5	>91	>99	29
0.3% Pd/hydroxyapatite	363	$PhCF_3$	5.8	84	−	327
H-K-OMS-2	383	$PhCH_3$	0.07	67	100	292

Table 12. Oxidation of 2-Adamantanol



catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	5	>99	>99	263
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	0.5	94	100	264
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	1.5	95	95	322
Ru−silicotungstate	373	$^{i}BuOAc$	20	98	99	347

4.4. Diols and Triols

Partial oxidation of various diols and glycerol to hydroxyacids and lactones, ketoacids, and hydroxyketones is a field of industrial interest. The reaction medium is water, and the precise control of pH or the amount of base is critical to achieve high selectivities. The performance of these catalysts is compared below in the oxidation of ethylene glycol and glycerol to monocarboxylates.

Ethylene glycol can be transformed quantitatively to glycolic acid by Pt/C when only 1 equiv of base is added and the actual oxygen concentration at the metal surface is kept low by working at reflux temperature in air (Table 15).[146] Supported Au seems to be a better choice: it combines an excellent rate with high selectivity.[205,208,227−230] The superior selectivity of gold has been shown also in the oxidation of propane-1,2-diol to lactate.[228]

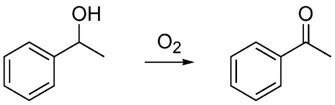
Supported Au nanoparticles are the catalyst of choice also for the oxidation of glycerol to glyceric acid (Table 16).[223,231] The activity of Pt/C is similar, but the selectivity is lower.

5. Conclusions

In this review, we have explored the heterogeneous catalytic methods available for the selective oxidation of alcoholic OH groups to carbonyl or carboxyl functional groups, using molecular oxygen as the only oxidant. A great number of new catalysts have been suggested in recent years for the "clean" oxidation of alcohols with molecular oxygen. Many of them are based on Ru and, to a smaller extent, on Pd species in various forms.

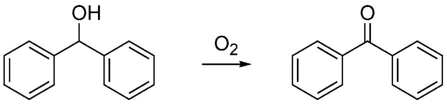
There are several catalysts that provide high yields in each class of the relatively simple test reactions discussed here. The selection of an appropriate catalyst may be based on other factors, such as the easy synthesis of the catalyst and its stability, sufficiently low C/S mass ratio, and high reaction rate (TOF). A closer inspection of the published data reveals that some catalysts possess surprisingly low activity, and for most reaction types they do not offer a real alternative to the conventional supported Pt-group metals—materials whose activity was discovered in the 19th century. The large number of patents reflects a considerable industrial interest in the application of supported (and promoted) Pt-group metal catalysts,

Table 13. Oxidation of 1-Phenylethanol to Acetophenone



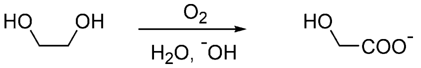
catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
1.4% Ru/Al_2O_3	356	$PhCF_3$	40	>98	>99	29
1.4% Ru/Al_2O_3	423	none	340	98	−	29
5% Pt−0.8% Bi/Al_2O_3	333	H_2O + detergent	340	97	>99	41
0.3% Pd/hydroxyapatite	363	$PhCF_3$	490	98	−	327
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	3.5	98	100	264
H-K-OMS-2	383	$PhCH_3$	0.5	99	100	292
Ru-Mg-Al-hydrotalcite	333	$PhCH_3$	0.5	100	100	302
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	6.2	100	100	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	3	98	98	322
$Pr_4N^+RuO_4^-$/ormosil(SiO_2)	348	$PhCH_3$	3	90	100	355
$Na_5PMo_{10}V_2O_{40}$/C	373	$PhCH_3$	4.5	94	100	346

Table 14. Oxidation of Diphenylmethanol to Benzophenone



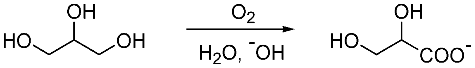
catalyst	T, K	solvent	TOF, h^{-1}	Y, %	S, %	ref
5% Pt−0.8% Bi/Al_2O_3	348	H_2O + detergent	700	99	100	41
Pd/resin	373	H_2O	0.9	85	–	82
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	295	$PhCH_3$	4	86	100	264
$Ru_{0.3}Co_2CeO_x$	333	$PhCF_3$	11	>99	>99	263
H-K-OMS-2	383	$PhCH_3$	0.5	100	100	292
Ru-Mg-Al-hydrotalcite	333	$PhCH_3$	1.2	100	100	302
Ru-Co-Al-hydrotalcite	333	$PhCH_3$	9.3	96	96	303
Ru^{3+}−hydroxyapatite	353	$PhCH_3$	3	>99	>99	322
Ru−silicotungstate	383	*t*-BuOAc	15	91	99	347

Table 15. Oxidation of Ethylene Glycol to Glycolate



catalyst	T, K	p_{O_2}, bar	TOF, h^{-1}	Y, %	S, %	ref
9% Pt/C	373	0.2	7	100	100	146
5% Pt/C	323	2	475	67	71	205
5% Pd/C	323	2	500	73	77	205
1% Au/C	343	2	1000	93	98	205

Table 16. Oxidation of Glycerol to Monocarboxylate at 333 K



catalyst	TOF, h^{-1}	Y, %	S, %	ref
1% Au/graphite	65	84	92	223
1% Au/C	100	56	100	223
5% Pt/C	105	47	74	223

dominantly in aqueous media. There are encouraging examples on the industrial acceptance of this green technology, though several other projects have been aborted due to unsatisfactory results. Obviously, replacement of stoichiometric and homogeneous catalytic oxidation methods by heterogeneous catalytic oxidations with molecular oxygen has already begun in the industry, though acceleration of this process necessitates more efficient solid catalysts.

Considering the topic from the point of view of substrate structure, the fast and selective oxidation of aliphatic and cycloaliphatic alcohols is certainly an unsolved problem. The difficulties are multiplied when more complex structures, such as polyfunctionalized and thermolabile alcohols, have to be oxidized. This area may be the most promising and rewarding field for future development.

6. Abbreviations

A% M/Y	metal (M) supported on Y, metal content (*A*) in wt %
A% M_1−*B*% M_2/X	bimetallic catalyst supported on a solid (X); metal content (*A*, *B*) in wt %
A% MO_x/Y	supported oxide; oxide content (*A*) in wt %
$A_xB_yC_z$...O_n	mixed oxide containing elements A, B, C
C/S	catalyst/substrate mass ratio
HAp	hydroxyapatite
HT	hydrotalcite
M^{n+}−X	solid material (X) containing M^{n+} ions in the matrix
OMS	octahedral molecular sieve
S	selectivity, in mol %
TOF	turnover frequency; molar ratio of converted substrate to the active component of the catalyst, per unit time (h^{-1}); it refers to the average rate at high conversion
X	conversion, in mol %
Y	yield, in mol %

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