Silver catalysts for liquid-phase oxidation of alcohols in green chemistry: Challenges and outlook

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ABSTRACT

Selective oxidation of alcohols allow using them as a key resource for obtaining of aldehydes, ketones, esters and carboxylic acids, which are valuable intermediates and high value products for the fine chemical, pharmaceutical and agrochemical industries. The high environmental impact of current technologies is driving the research of greener processes in the liquid phase. Most of this research is devoted to study catalytic systems based on platinum group metals and gold. However, despite their high levels of activity, these catalyst systems are quite expensive and suffer of deactivation and stability problems. Silver-containing catalysts may be their excellent alternative. They are the basis for a number of important industrial oxidation processes in the gas-phase. However, research on its use for liquid-phase processes is quite limited, especially for selective oxidation of alcohols.

Therefore, this short review focuses on the systematization and analysis of the available literature data on the liquid phase oxidation of alcohols using silver-containing catalysts with the aim of identifying the problems and limitations of the state of the art and the prospects of further studies and practical implementation of such systems for the target processes.

1. Introduction

Selective oxidation of alcohols is one of the most important processes in production of chemicals and fine organic synthesis because carbonyl compounds (aldehydes, ketones) are important intermediates for the production of polymers, pharmaceuticals, vitamins and dyes, and are also used as solvents, perfumes, and flavoring agents. Annual production of carbonyl compounds is over 100 million tons, and many of these compounds are obtained by oxidation of alcohols [1]. Traditional methods of obtaining carbonyl compounds are based on the use of stoichiometric oxidants, which are mostly oxides of transition metals and their salts, halogen-containing compounds. Tough environmental and economic requirements dictate the urgent need for new technology in fine organic synthesis, to replace the current stoichiometric processes that lead to the formation of large amounts of toxic waste. The greatest interest in this respect are catalytic methods for producing oxygen-containing compounds, based on the use of products from biomass processing as raw material, and environmentally friendly and cheap oxidants, such as molecular oxygen or air. Processing of biomass generates large amounts of by-products (alcohols, terpenes, etc.) which

transformation into commercial products is one of the most important and promising tasks of "green chemistry". Selective liquid-phase oxidation of these products to obtain carbonyl and carboxyl compounds on heterogeneous catalysts is one of the most promising ways to solve this problem. In addition of the use of renewable feedstocks, adaptation of such production processes to the principles of green chemistry [2] requires: prevention of waste (namely, avoiding the use of stoichiometric oxidants and added bases), atom economy (namely, incorporating all the C atoms from the substrate and the atoms from the oxidant into the final useful product), as well as to be designed for energy efficiency, (namely, using the lowest possible reaction temperature and pressure, which leads towards operating in liquid-phase and atmospheric pressure). However, implementation of these processes would be impossible without the creation of novel efficient catalytic systems with high activity and selectivity.

A number of catalysts based on supported Pt and Pd have been proposed in the literature for liquid-phase oxidation of alcohols [3–18]. However, despite their high activity, these catalytic systems show insufficient selectivity for the target products, are very sensitive to catalytic poisons and the oxidant, deactivate rapidly and are very

expensive. Early works in the 90's [4] assumed that the oxidation of the alcohol took place on metallic centers (Pt°) and that their deactivation was caused by their over oxidation by oxygen, due the strong oxidizing ability of Pt and Pd. However, in situ XAFS and XPS studies of Pd catalysts revealed electron deficient Pd^{2+} present in surface PdO as the active site for reaction, and that, in fact, the transformation of the oxide into the metal is the cause, and not result, of catalyst deactivation [10]. Its activity depends on the Pd metal loading, dependency that is directly linked to the Pd dispersion and associated degree of surface oxidation (higher for the more dispersed metal) [12]. The poor performance of metallic Pd can be due to stronger adsorption of by-products. A similar trend (activity dependent on metal surface dispersion and its related degree of oxidation) been reported for Pt catalysts [16]. As a consequence, in polyfunctional alcohols Pd and Ru catalysts can promote intra- and intermolecular hydrogen transfer (isomerization and hydrogenation), which reduces selectivity to the desired carbonyl product [16]. Furthermore, oxidation of primary alcohols over Pt is prone to produce carboxylic compounds which can strongly adsorb on the Pt surface, thus breaking the catalytic cycle. To avoid this, in many Pt catalyzed oxidation reactions, bases (e.g., K_2CO_3 or NaOH) must be added to ensure that the reaction can go smoothly [4].

The surprisingly high activity of gold nanoparticles (Au NPs) for oxidation at low temperatures caused a huge interest of scientists on this type of catalysts. Supported gold catalysts exhibit higher activity and selectivity in liquid-phase oxidation reactions than other noble metals catalysts, such as Pt and Pd [19–35]. However, gold catalysts still face a number of unsolved problems. Firstly, only gold nanoparticles smaller than 5 nm exhibit high activity; even more, according to several research groups (including the authors of this work) gold clusters smaller than 2 nm are the most active [36–39], while larger particles are virtually inactive at low temperatures. This phenomenon imposes very strict requirements for the methods of preparing gold catalysts to get Au NPs of the smaller sizes and to avoid their coalescence. Another important and unresolved issue of gold catalysts is their rapid deactivation, both at work and during storage, which is a serious problem for their practical application [40–47].

Though inferior in activity of supported nanogold in a number of processes at low temperatures, such as CO oxidation [48–53], silver catalysts are much stable and cheaper than gold-containing systems and very active in many selective oxidation reactions. Silver catalysts are the basis of two of the main petrochemical oxidation processes by world production capacity: epoxidation of ethylene [54] and production of formaldehyde by oxidation of methanol [55]. The catalytic oxidative power of Ag is due to its ability to chemisorb oxygen in atomic form [56]. The atomic oxygen could fit into the octahedral holes of Ag and cause the accumulation of oxygen within the bulk of silver [57]. Silver catalysts are also excellent for many reactions of gas-phase oxidation, such as selective catalytic reduction of NO_x [58], selective oxidation of ammonia [59], oxidation of methane [60], oxidation of styrene [61], and also gas-phase selective oxidation of alcohols other than methanol, such as ethanol [62–66], benzyl alcohol [67–69] or ethylene glycol [70], as well as dehydrogenation of ethanol [14]. Despite this, surprisingly, there are very few works devoted to liquid-phase oxidation of alcohols on catalyst systems based on silver, as shown below.

Therefore, the objective of the present review is to identify and discuss the challenges and outlooks of the use of (nano)silver-based catalytic systems as a potential alternative to noble metal based catalysts for oxidation of alcohols in the liquid-phase. To reach this goal, we made a systematic analysis of the available literature data on this reaction using silver-containing catalysts, with special attention to their sustainability issues (prevention of waste, atom economy and energy efficiency).

2. Liquid phase oxidation of alcohols

Despite the scarce number of publications on the use of silver-based catalysts for this type of reaction, this information is unsystematic and very scattered on two aspects, catalytic systems and reactions studied. For this reason, the more relevant results in literature, summarized in Table 1, will be discussed grouping them by the type of catalyst.

Table 1
Selective oxidation of alcohols on silver catalysts.

Catalysts	Substrate (alcohol)	Oxidant	P (bar)	T (°C)	Solvent	Time (h)	Conversion[a] (%)	Selectivity (%) ketone/aldehyde	acid	ester or ether[#]	Ref.
$AgNO_3 + Na_2CO_3$	phenylmethanol	air	1	111	toluene	6		96[b]			[71]
$AgNO_3 + Na_2CO_3$	4-methoxybenzyl alcohol	air	1	111	toluene	6		99[b]			[71]
$AgNO_3 + Na_2CO_3$	4-chlorobenzyl alcohol	air	1	111	toluene	24		52[b]			[71]
$AgNO_3 + Na_2CO_3$	4-bromobenzyl alcohol	air	1	111	toluene	24		63[b]			[71]
$AgNO_3 + Na_2CO_3$	4-nitrobenzyl alcohol	air	1	111	toluene	24		67[b]			[71]
$AgNO_3 + Na_2CO_3$	4-fluorobenzyl alcohol	air	1	111	toluene	5.5		97[b]			[71]
$AgNO_3 + Na_2CO_3$	benzhydrol	air	1	111	toluene	6		96[b]			[71]
$AgNO_3 + Na_2CO_3$	1-(naphthalen-2-yl) ethanol	air	1	111	toluene	24		90[b]			[71]
$AgNO_3 + Na_2CO_3$	2-phenylethanol	air	1	111	toluene	12		0[b]			[71]
$AgNO_3 + Na_2CO_3$	cyclohexanol	air	1	111	toluene	12		4[b]			[71]
$AgNO_3 + Na_2CO_3$	1-octanol	air	1	111	toluene	12		3[b]			[71]
$AgNO_3 + Na_2CO_3$	2-octanol	air	1	111	toluene	12		6[b]			[71]
$AgNO_3\text{-}SiO_2$ [c]	cyclododecanol		1	121	C_2Cl_4	2	8	0			[72]
$AgNO_3\text{-}SiO_2$ [c]	cyclododecanol		1	76	CCl_4	2	99	57			[72]
$AgNO_3\text{-}SiO_2$ [c]	cyclododecanol		1	68	n-hexane	2	19	84			[72]
$AgNO_3$ [c]	cyclododecanol		1	76	CCl_4	2	2	100			[72]
Ag_2CO_3/Celite [c]	phenols		1	80	benzene	0.5 - 2		< 90[d]			[74]
Ag_2CO_3/Celite [c]	p-hydroxy-diphenylamine		1	25	CH_2Cl_2	0.16		97[e]			[74]
Ag_2CO_3/Celite [c]	o-aminophenol		1	40	CH_2Cl_2	0.25		33[f]			[74]
Ag/pumice [g]	phenylmethanol	O_2	2	60	CH_3CN		0.8[i]	100			[76]
Ag/pumice [h]	phenylmethanol	O_2	1	75	CH_3CN		4.5[i]	100			[76]
RH-Ag	phenylmethanol	air	1	205	no	1	1	93		7[#]	[77]
RH-Ag	phenylmethanol	O_2	1	205	no	1	10	17		83[#]	[77]
RH-Ag(C) [h]	phenylmethanol	air	1	205	no	1	14	5		95[#]	[77]
RH-Ag(C) [h]	phenylmethanol	O_2	1	205	no	1	21	33		67[#]	[77]

(continued on next page)

Table 1 (*continued*)

Catalysts	Substrate (alcohol)	Oxidant	P (bar)	T (°C)	Solvent	Time (h)	Conversion[a] (%)	Selectivity (%)			Ref.
								ketone/ aldehyde	acid	ester or ether[#]	
Ag/SiO$_2$ + CeO$_2$ (2:1)	phenylmethanol	O$_2$	1	140	xylene	2	98	95			[78]
Ag/SiO$_2$ + CeO$_2$ (2:1)	1-octanol	O$_2$	1	140	xylene	0.75	29	90			[78]
Ag/SiO$_2$ + CeO$_2$ (2:1)	2-octanol	O$_2$	1	140	xylene	2	63	> 99			[78]
Ag/SiO$_2$ + CeO$_2$ (2:1)	cyclohexanol	O$_2$	1	140	xylene	2	22	71			[78]
Ag/SiO$_2$ + CeO$_2$ (2:1)	1-phenylethanol	O$_2$	1	140	xylene	0.75	> 99	> 99			[78]
Ag/Al$_2$O$_3$ [j]	crude glycerol	O$_2$	5	60	water + NaOH (NaOH/Gly = 4)	1.2	10		GA 50 GLYCA 27 FA 18		[79]
Ag/Al$_2$O$_3$ [j]	pure glycerol	O$_2$	5	60	water + NaOH (NaOH/Gly = 4)	0.25	10		GA 28 GLYCA 36 FA 35		[79]
						2	30		GA 27 GLYCA 45 FA 28		
Ag/Al$_2$O$_3$ [k]	pure glycerol	O$_2$	5	60	water + NaOH (NaOH/Gly = 4)	3	85		GA 10 GLYCA 57 FA 31 [l]		[80]
AgNPs/GOSH + NHPI	phenylmethanol	O$_2$	1	80	acetonitrile	24	61	58	13	29	[81]
Ag/TiO$_2$	1-octanol	O$_2$	1	80	n-heptane	6	2.5	90	8	4	[82]
Ag/CeO$_2$/TiO$_2$	1-octanol	O$_2$	1	80	n-heptane	6	12	92	3	5	[82]
Ag/Fe$_2$O$_3$/TiO$_2$	1-octanol	O$_2$	1	80	n-heptane	6	8	100	0	0	[82]
AgMPAV [m]	cinnamyl alcohol	O$_2$	1	90	toluene	10		93[b]			[83]
AgMPAV [m]	crotyl alcohol	O$_2$	1	90	toluene	14		90[b] - 88[b,n]			[83]
AgMPAV [m]	allylcarbinol	O$_2$	1	90	toluene	24		60[b]			[83]
AgMPAV [m]	2-cyclohexenol	O$_2$	1	90	toluene	16		70[b]			[83]
Ag-doped MnO$_2$	phenylmethanol	O$_2$	1	100	toluene	2	100	> 99			[84]
Ag-OMS-2	1-phenylethanol	TBHP	1	75	acetonitrile	4	80	90			[85]
Ag-OMS-2	cyclohexanol	TBHP	1	75	acetonitrile	4	90	90			[85]
Ag-OMS-2	benzhydrol	TBHP	1	75	acetonitrile	4	80	84			[85]

GOSH: thiolated graphene oxide.

NHPI: N-hydroxyphthalimide.

FA: formic acid; GA: glyceric acid; GLYCA: glycolic acid.

n.a. - not analyzed/not applicable.

RH: porous silica from rice husk.

TBHP: tert-butyl hydroperoxide.

OMS-2: cryptomelane-type octahedral molecular sieve.

[a] Alcohol conversion.

[b] Data of yield instead of selectivity are given.

[c] Non-catalytic redox reaction.

[d] Yield of their corresponding quinones.

[e] Yield of quinone monoanil.

[f] Yield of dimeric phenoxazone.

[g] As-prepared.

[h] After calcination at 500 °C.

[i] Specific rate constant k (mol h^{-1} g$_M^{-1}$) instead of conversion.

[j] Supported on partially hydrated gamma alumina.

[k] 3.6 wt.% Ag supported on basic alumina; preparation details in text.

[l] Plus 1% oxalic acid.

[m] Silver exchanged vanadium-containing molybdophosphoric acid.

[n] After third cycle.

2.1. Silver salts as catalysts

Wang et al. [71] investigated AgNO$_3$ as a catalyst for the selective oxidation of allylic and benzylic alcohols using air as the oxidant. The reaction did not proceed in argon atmosphere nor in the absence of a base in reaction mixture. The use of a weak inorganic base (Na$_2$CO$_3$) provided higher yield of aldehyde than that of strong inorganic (NaOH) or organic (NEt$_3$) bases. After systematic studies the authors selected the optimal conditions of the process (the highest yield of reaction products): 2 mol% of AgNO$_3$ catalyst, 2 eq. of Na$_2$CO$_3$ base in toluene under reflux (111 °C), and air atmosphere as oxidant. The reuse of the catalyst reduced the product yield by 20 and 55% in the second and the third run, respectively. The catalyst was also efficient to oxidize a range

of substituted benzyl and allyl alcohols. To determine the possible re-action mechanism using the AgNO$_3$/Na$_2$CO$_3$ system, the used catalyst was filtered after the catalytic test, and investigated by TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy). They revealed Ag nanoparticles (Ag NPs) well dispersed on the carbonate and two silver species (Ag$^+$ and Ag°). Thus, during the reaction, Ag$^+$ species formed from AgNO$_3$ are reduced by the alcohol with formation of metallic Ag° nanoparticles that are deposited on the surface of Na$_2$CO$_3$. These Ag NPs may also be formed from Ag$_2$CO$_3$ formed by interaction of Ag$^+$ species with Na$_2$CO$_3$. Based on these results, the authors proposed that alcohol oxidation occurs on the Ag NPs; after its adsorption on the silver surface, the alcohol is dehydrogenated and the aldehyde is formed by interaction with the

carbonate and molecular oxygen. The decrease of products yield upon repeated use of the catalytic system occurs due to the formation of Ag_2CO_3 (a higher degree of ionization of $AgNO_3$ makes it more effective than Ag_2CO_3), and/or aggregation of Ag nanoparticles and/or loss of Ag during the procedure of extraction of the catalyst from reaction medium.

It should be noted that earlier studies reported that silver carbonate supported on silica [72] or celite [73–75] can be used as stoichiometric and mild oxidizing agents for the selective oxidation of alcohols. Kakis et al. [75] studied thoroughly the mechanism of alcohols oxidation by silver carbonate on celite, the nature of transition state, the influence of surface adsorption and solvent composition and possible impact of intermediate reaction products. According to the proposed mechanism, the alcohol is reversibly adsorbed forming a covalent bond to silver ions, and then a concerted irreversible shift of electrons generates reduced silver atoms and the carbonyl compound precursor, that lead to the products according to the reaction: $R_2CHOH + Ag_2CO_3 \rightarrow R_2C=O + H_2O + 2Ag + CO_2$. This points out that during the catalytic reaction part of the product is produced by the stoichiometric oxidation and that in the absence of gaseous oxidant the catalyst is irreversibly deactivated by decomposition of the carbonate. This phenomenon may be contributing to the progressive loss of activity in the successive reuse of the catalyst. The main drawbacks of this approach are the use of sodium carbonate, which will lead to formation of undesirable by-products and waste, and the progressive loss of activity when catalyst is reused.

2.2. Supported Ag catalysts

Liotta et al. [76] studied the selective oxidation of benzyl alcohol to benzaldehyde on pumice-supported bimetallic Pd-Ag (0.27 and 0.13 wt. %, respectively) and monometallic Pd (0.27 wt.%) and Ag (0.6 wt.%) catalysts, in autoclave at 60 °C under 2 atm of oxygen. As aldehyde concentration increased linearly with run time, the zero order specific rate constant was used as an indicator of activity. The influence of oxidizing (air) and reducing (H_2) pretreatments at 350 °C on their catalytic activity was studied at 75 °C under oxygen flow at atmospheric pressure. Among the as-prepared catalysts, the most active, with 95% selectivity to benzaldehyde, was Pd/pumice, where palladium was present as $Pd°$ and Pd^{2+}. The atmosphere of pre-treatment did not affect the activity of the Pd catalyst, with the exception of a small increase in activity after its pre-reduction, though the only or the main electronic state was Pd^{2+}. The introduction of Ag as the second metal, accompanied by electronic transfer between the two metals that kept palladium in the metallic state, caused a reduction of the activity of the as prepared catalyst, while Ag/pumice showed the lowest activity. Conversely to monometallic Pd catalyst, activity of Pd-Ag/pumice increased with each consecutive calcination pretreatment, and reached its best value after a consecutive calcination in air at 500 °C, a treatment that also boosted the activity of the monometallic Ag catalyst. Based on XRD and XPS data of catalysts before tests, the authors attributed these activity increases to presence of highly dispersed metallic $Pd°$ and $Ag°$ atoms, respectively, which they considered the most active sites. Interestingly, the specific activity of the physical mixture of most active Pd/pumice and Ag/pumice catalysts was between two- and threefold higher that the addition of those of their monometallic catalysts components and even fourfold higher than that of the bimetallic PdAg catalyst with the same metallic loadings. The authors explained this by the presence of a synergistic effect between $Ag°$ and $Pd°$, which consists in that silver plays an important role in the activation of oxygen while palladium activates the alcohol molecules. The lower activity of the bimetallic catalyst was ascribed to the massive presence of PdO, probably stabilized by silver. However, in light of later studies of supported Pd catalysts [10,12], an alternative explanation may be proposed: while in the physical mixture, palladium is in its optimal oxidation state (Pd^{2+}) in the bimetallic catalyst the electronic transfer from Ag keeps it in the less active metallic state ($Pd°$).

Adam et al. [77] investigated silica obtained from rice husk (RH) modified with silver by coprecipitation (RH-Ag) and its calcined form (RH-Ag(C)) as catalysts for selective oxidation of benzyl alcohol. XRD, FTIR and TEM results showed that silver was present in the metallic state, distributed not homogeneously in the silica matrix, which had mesoporous channels in a regular arrangement. Activity of the calcined RH-Ag(C) was higher, which was due to the lower amount of residual carbon in the solid. Alcohol conversion (C_{ROH}) was much higher when using pure oxygen as oxidant than when using air, and conversion varied with run time and passed through a maximum at 3 h. Unexpectedly, the major product on both silver catalysts (RH-Ag and RH-Ag(C)) was dibenzyl ether (selectivity > 71%), the other product being benzaldehyde, which selectivity increased with run time when using RH-Ag(C). The authors proposed that each product was formed by a different mechanism, but both proceed on silver centers. In the reaction conditions selected by the authors as optimal (0.3 g catalyst, 20 mL alcohol under reflux, no solvent), RH-Ag(C) reached the maximum conversion (31%) with 72% selectivity to ether using oxygen atmosphere, or 21% conversion with 94% selectivity to ether using air. However, reaction with oxygen in the absence of catalyst or in the presence of unmodified silica RH reached 11–13% conversion, giving only benzaldehyde (> 99% selectivity), i.e., a benzaldehyde yield higher than in the presence of the silver catalyst. It is noteworthy that even in the absence of oxidant, conversion reached 7% and the main product on RH-Ag(C) was dibenzyl ether (87% selectivity). This might put into question the role of silver in the formation of benzaldehyde on this system, while ether formation was clearly related to silver centers. Nevertheless, despite of a number of physicochemical methods (XRD, SEM, TEM, EDX, FTIR, BET) were used, the nature of active sites of catalysts could not be identified.

Beier et al. [78] investigated selective oxidation of benzyl alcohol on a number of supported Ag catalysts, prepared by impregnation of SiO_2, TiO_2, Al_2O_3, celite, CeO_2, MgO, kaolin, and several activated carbons, using a special screening approach based on the testing of physical mixtures of catalysts. Their activity was tested using xylene as solvent, under reflux, and oxygen flow at atmospheric pressure, in the absence of a base, and was compared after 1 h of reaction to avoid the influence of deactivation. Although separately Ag/SiO_2 and CeO_2 were practically inactive (C_{ROH} < 10%), their physical mixture was very active (C_{ROH} = 98% with 95% benzaldehyde selectivity); so, they investigated the collaborative behavior of the $Ag/SiO_2 + CeO_2$ system. Catalytic activity strongly depended on the ratio $CeO_2/Ag–SiO_2$ in the mixture, the Ag content in $Ag–SiO_2$ (with a maximum C_{ROH} for 10 wt.% Ag) and the catalyst calcination procedure and temperature. TEM, XRD and X-ray absorption spectroscopy (XANES, EXAFS) data of the catalysts showed that silver was present mostly as metallic particles, but the authors suggest that oxygen species incorporated in the silver lattice (β-oxygen) appear to be important in the mechanism of the alcohol oxidation. It should be noted that, based on the amount of O_2 uptake and the diffuse reflectance spectra of supported Ag catalysts, Yamamoto et al. [67] inferred that oxidized surface Ag species on the metallic Ag were the active Ag components for the gas-phase partial oxidation of benzyl alcohol. The optimal calcination temperature (T_C) was 500 °C. In situ XANES spectra showed that below that T_C oxidized forms of silver are not reduced to metallic species, while at higher T_C, oxygen dissolved in metallic Ag phase evaporated. The role of cerium was to activate the molecular oxygen. Noticeably, this combined $Ag/SiO_2 + CeO_2$ catalytic system exhibited an activity for oxidation of benzyl alcohol superior to that of supported Pd and Au catalysts, even if these latter are mixed with CeO_2. In addition, the same catalytic system was very active and selective for the oxidation of other substituted benzyl, primary and secondary alcohols under similarly soft conditions (10 wt.% Ag/SiO_2 to CeO_2 ratio = 2, solvent xylene, reflux in O_2 atmosphere). Nevertheless, the catalyst suffered a serious drawback: the used catalyst lost 84% of its activity, a loss caused by the water produced by the reaction itself, and this deactivation was irreversible, as a new calcination at 500 °C in

O_2 only recovered 45% of the original activity.

Skrzynska. et. al [79]. compared the activity of four different noble metals (Ag, Au, Pd and Pt) supported on Al_2O_3 in the liquid phase oxidation of pure glycerol (Gly) and 'crude glycerol', at 60 °C under 5 bar oxygen and in the presence of base (NaOH/Gly molar ratio = 4). Crude glycerol (47.4 wt.% Gly, 29.1 wt.% CH_3OH, 8.6 wt.% H_2O, 1.3 wt.% of ash and 13.6 wt.% of matter organic, non-glycerol and non-methanol (MONG-NM)) is the direct by-product from biodiesel production and its use as raw material is of industrial interest, as it would save its expensive purification process. In the initial period of reaction, the most active catalyst was Au/Al_2O_3, using either pure or crude glycerol. Taking the value for pure Gly on Ag/Al_2O_3 as reference, the relative initial reaction rates for the Au, Pt, Pd and Ag catalysts using pure Gly were for 15, 3.3, 1.5 and 1, respectively. These big differences were ascribed as due to their metallic particles distribution, broader and with bigger sizes for the silver catalyst (21.2 ± 18.6 nm) than for the others (narrow distribution with average diameters of 3–4 nm). Interestingly, while the other metals favored a non-destructive oxidation to tartronic acid via glyceric acid, Ag/Al_2O_3 promoted the oxidative cleavage of Gly molecule leading directly to glycolic (2-hydroxyethanoic) and formic acids (35.9% and 35.3% selectivity at C_{ROH} = 10%, respectively), while the three other metals favored a non-destructive oxidation to tartronic acid via glyceric acid (Scheme 1). However, those relative initial rates and their differences became much smaller when shifting to 'crude glycerol': 1.42, 0.96, 0.26 and 0.44, respectively, for the same catalysts. This means that Ag/Al_2O_3 catalyst was much more resistant towards the impurities than Au, Pt and Pd catalysts (60% drop of activity vs. 90, 71 and 81%, respectively). At the variance of the other catalysts, when crude glycerol was used, there was a drastic modification of Ag/Al_2O_3 selectivity: a substantial increase in the selectivity to glyceric acid (ca. 50%), the direct oxidation product, and a reduction of the oxidative cleavage products. XPS analysis showed that the deposited metals were in a totally reduced state in all the catalysts, both before and after the reaction, and no change on the surface metal/Al ratio was observed after the reaction.

The high selectivity to glycolic acid observed on the silver catalyst motivated the authors to further deepen the study of Ag/Al_2O_3 catalysts performance for these reactions [80]. The effects of the preparation method (type of solvent and reductant used), Ag loading (from 0.7 to 3.6 wt.%), amount of base added (molar ratio NaOH/Gly from 0 to 4) and type of alumina support (phase composition, basicity) on the properties and the activity of the catalysts were evaluated. The preparation by the chemical reduction method in a basic methanol solution, using formaldehyde as a reductant, gave the most active catalyst. Catalysts were practically inactive in the absence of a base (maximum C_{ROH} after 120 min at 100 °C was 0.5%), and the NaOH/Gly ratio was a determining factor for the total activity. Reaction rates decreased with run time, leading even to a conversion plateau in some cases, which was attributed to the decrease of pH caused by the acidic products. Once reached such plateau, further addition of fresh NaOH to the reaction mixture clearly rebooted the conversion process without affecting the selectivity. Particle size distributions were broad and very different depending on the preparation method. Contrary to the general consensus that smaller particles provide higher activity, among similarly prepared catalysts the highest activity was observed with the catalyst with the biggest average particle diameter (31.8 nm) and it decreased with the decrease of particle size. Nevertheless, one must take into account that in such broad particle size distribution not necessarily particles of all sizes are catalytically active, as observed for CO oxidation on Ag catalysts [52,53]. Selectivity to glyceric acid followed the opposite trend with the decrease of particle size. In addition, the nature of the support also played a key structural role: changing the support from basic activated alumina to acidic or gamma alumina completely altered the most important physicochemical properties of the catalyst, such as the oxidation state of the silver nanoparticles, their mean particle diameter and distribution, as well as their performance in the glycerol oxidation process. Authors suggested that the most active catalysts are those in which silver is completely reduced to a metallic state. The characteristic high selectivity to glycolic acid of Ag catalysts in this reaction increased significantly with the increase of metal loading.

As a whole, the most active catalysts were also the most selective to glycolic acid. The best results in terms of conversion and selectivity to glycolic acid (57.1% selectivity at C_{ROH} = 85%) were achieved after 3 h at 60 °C under 5 bar of oxygen pressure over a 3.6 wt% Ag catalyst supported on basic activated alumina. In addition, the Ag/Al_2O_3 catalysts showed good stability in the continuous operation mode and very good resistance to the impurities present in a crude glycerol fraction. Despite the large amount of studies and interesting results, it should be noted that the reaction conditions used by the authors (high NaOH to alcohol ratio and high pressure) do not meet the requirements of green chemistry.

Looking for a high dispersion of Ag NPs, Zahed et al. [81] explored the use of graphene oxide and its modification to understand the support effect on their activity. The oxygen-containing functional groups on the basal plane of GO can act as nucleation sites of metal nanoparticles. They synthesized catalysts based on Ag NPs, immobilized on graphene oxide either fully reduced (rGO), partially reduced (denoted GO), or thiolated partially reduced (GOSH) and tested them for aerobic oxidation of benzyl alcohol (0.4 M in acetonitrile, 80 °C, 1 atm O_2). AgNPs/GOSH catalyst showed the highest activity with C_{ROH} = 61% in 24 h (58% selectivity to benzaldehyde), but such activity could be achieved only in presence of a radical initiator, N-hydroxyphthalimide (NHPI), as co-catalyst. In absence of NHPI, conversion was 90% lower. To stabilize Ag NPs, support must be functionalized: completely reduced rGO turned out to be an unsuitable support for Ag NPs, leading to Ag particles of 40–150 nm. Thiolated graphene oxide ensured uniform distribution and stabilization of Ag NPs (of 5–15 nm) and prevented aggregation and leaching of immobilized Ag NPs. Thus, the authors attributed the superior catalytic activity of AgNPs/GOSH to better stabilization and distribution of Ag NPs, caused by the strong interaction between GOSH and Ag NPs. Despite the advantages of the very soft conditions used, the main drawback of this catalytic system is the need of the homogenous co-catalyst (NHPI) in a high amount (mol ratio alcohol/NHPI = 2), that will inevitably lead to difficulty of removal and formation of undesirable by-products.
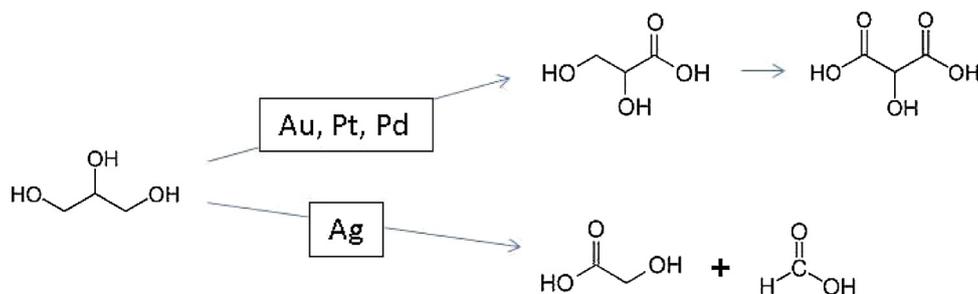
Scheme 1. Main products of the selective oxidation of glycerol on alumina supported metals according to [79,80].

Our research teams investigated nanoparticulated Ag supported on titania (Ag/TiO$_2$) and their modifications as catalysts for selective oxidation of the less reactive alcohols under conditions close to requirements of "green chemistry", using 1-octanol as model molecule, and comparing them to their Au/TiO$_2$ homologues [82]. The activity of catalysts in its aerobic selective oxidation was tested using nontoxic solvent (heptane), absence of alkaline additives and initiators, a pressure of 1 atm, and low temperature (80 °C). Under these conditions activity of as-prepared Ag/TiO$_2$ was relatively low, (C$_{ROH}$ = 2.5% after 6 h, with 90% selectivity to octanal), lower than that of Au/TiO$_2$. To improve it, redox pretreatments and the modification of the support surface were explored as an approach to regulate the structural and electronic properties of deposited silver. The titania support was modified with oxides MxOy (M = Ce, Fe or Mg) deposited on by impregnation in molar ratio Ti/M = 40. The effect of these two strategies in the two systems was different: performance of gold untreated catalysts was not affected by the modification of support, but was boosted by reductive pretreatment, while that of silver catalysts was boosted by some support additives but damaged by both reductive and oxidative pretreatments. Support modification with Ce, Mg and Fe increased conversion by a factor or 5, 3 and 2.5 times, respectively, without modifying the product distribution (octanal selectivity > 90%). This makes these catalysts more selective to aldehyde (at isoconversion) than their respective nanogold homologues. Octanal is the most expensive and sought-after product of n-octanol oxidation. Characterization by FTIR CO, HRTEM, XPS and H$_2$ TPR, showed that support modifiers influenced the structural and electronic properties of Au and Ag species through a metal-support and metal-modifier interaction and that the order of catalytic activity (Ag/CeO$_2$/TiO$_2$ > Ag/Fe$_2$O$_3$/ TiO$_2$ > Ag/MgO/TiO$_2$ > Ag/TiO$_2$) was the same than that of the proportion of Ag atoms present as ionic Ag$^+$ species in the catalysts The detrimental effect of redox pretreatments was accompanied by a decrease of the proportion of these ions. This allowed to conclude that Ag$^+$ ions were the active sites for this reaction, and that the effects of the nature of support modifiers and pretreatment atmosphere on catalytic properties of Ag-containing systems is determined primarily by the action of these factors on the electronic state of the deposited silver. The results evidenced the potential of nanosilver catalysts for the liquid phase oxidation of alcohols under mild conditions, keeping in mind that 1-octanol was selected as the model of the least active ones, and that activity can be improved by selecting the optimum modifier.

2.3. Ag-doped oxide catalysts

Nagajaru et al. [83] investigated catalysts based on the modification of Kegging-type 12-molybdophosphoric acid (MPA) with Ag and V for selective oxidation of allylic alcohols using molecular oxygen as an oxidizing agent. When they used cinnamyl alcohol as model molecule, the best results (93% yield of aldehyde in 10 h) were obtained when the catalyst contained both V and Ag, i.e., Ag$_{1.64}$H$_{2.36}$PMo$_{11}$V$_1$O$_{40}$, using a solution of 0.2 M alcohol in toluene under reflux, in the presence of molecular oxygen under atmospheric pressure. The authors attributed the higher catalytic activity of this sample, compared to the monosubstituted ones, to the synergistic effect between silver cationic sites (Ag$^+$) and redox active sites of vanadium (V^{5+}), where Ag activates molecular oxygen and V oxidizes the substrate through the transfer of electrons and protons; however, no characterization evidence supporting this hypothesis was provided. The catalyst retained its activity for three cycles. Elemental analysis of the content of Ag and V in used samples after the third run evidenced that almost no leaching of active component took place during the catalytic process. The catalyst was claimed to be reusable, economical, non-corrosive and ecologically safe.

Adil et al. [84] investigated oxidation of benzyl alcohol and its 4-substituted derivatives (0.2 M in toluene, 100 °C, 2 h) using molecular oxygen as oxidant (20 cm^{3}min^{-1}) on catalysts based on manganese

oxide doped with silver nanoparticles prepared by coprecipitation and studied the influence of Ag content (1–5 wt.%) and calcination temperature (300–500 °C). Both parameters and catalyst specific surface area played an important role. Activity decreased with increasing Ag content. No silver containing phase was detected by XRD, which also showed that manganese oxide phase composition depended on T$_C$. The crystallite size ranges of the catalysts calcined at 400 °C with 1, 3 and 5% Ag were 0.4–2.8, 13.7–16.1 5.1–15.8 nm, respectively. The best performance (C$_{ROH}$ ~100% with 99% selectivity to benzaldehyde) was observed for 1% Ag-MnO$_2$ catalyst calcined at 400 °C, and attributed to the presence of tetragonal β-MnO$_2$. The authors attribute the lower activity after calcination at higher or lower T$_C$ to the formation of different Mn oxide phases. However, the surface area of this catalyst (78 m^{2}g^{-1}) was more than twofold that of same composition calcined at T$_C$ = 300 °C (32 m^{2}g^{-1}), which shows C$_{ROH}$ = 98.6% and where the present phases were MnCO$_3$ and tetragonal α-MnO$_{0.93}$; this puts into question the role of that manganese oxide phase. In fact, the most active catalyst was the less crystalline one. The absence of surface area data of catalysts with different Ag contents does not allow to deepen the analysis of the effect of this parameter. A range of benzyl alcohol derivatives substituted in C4 were also converted using the best catalyst, with C$_{ROH}$ > 70% to corresponding aldehydes with selectivity > 99% for all the investigated alcohols. The authors mention that activity was very low with aliphatic alcohols, without providing any data. Regretfully, the authors focused on studying of catalytic properties, without any attempt to explain the nature of active sites. Thus, no information on the role of silver for the high catalytic activity was provided.

Yadav and Yadav [85] investigated selective oxidation of secondary alcohols to ketones with tert-butyl hydroperoxide (TBHP) on a related catalyst, based on silver (15% wt.%) incorporated in a cryptomelane-type octahedral molecular sieve (OMS-2), previously found active for the gas phase oxidation of 1-octanol to octanal [86]. This Ag/OMS-2 catalyst had a nanofibrous crystal structure with a large specific surface area. After investigating various factors influencing the reaction rate and conversion (amount of catalyst, reaction temperature, stirring rate, silver content, solvent and oxidant nature, etc.) using 1-phenylethanol as model molecule, they found that the best conditions to get the highest conversion (C$_{ROH}$ = 80%) in 4 h were: 0.2 M solution in acetonitrile, 75 °C, alcohol/TBHP mole ratio of 1:3, speed of agitation 900 rpm, catalyst loading of 0.012 g/cm^3. For all the investigated alcohols (substituted 1-phenylethanols, cyclohexanol), the conversion was > 75% with a > 90% selectivity to the corresponding ketone, though using longer reaction times. In Ag-OMS-2 catalyst, manganese exists in mixed valency Mn^{3+} (Mn$_2$O$_3$) and Mn^{4+} (MnO$_2$), and Ag$^+$ ions are incorporated in the tunnel structure of OMS-2 and get converted to Ag^{2+} ions by interaction with Mn ions [87]. This causes an important improvement of the reducibility of the Mn oxide [86]. Thus, the authors suggested that the synergistic effect among Ag, Mn and K ions was responsible for the enhancement in the activity of catalyst. In addition, the catalyst fully retained its activity after five cycles. The main drawback of this approach is the use of TBHP as oxidizing agent, because it is flammable and explosive, has irritating effect, affects central nervous system, lungs, has mutagenic and embryotoxic effects, may penetrate body through intact skin; in addition, its use leads to formation of undesirable by-products (tert-butanol).

It should be noted that in these systems silver is not forming an individual phase but is integrated as a cationic component inside a foreign oxidic crystalline network. So, these cases may be considered borderline of the scope of the present review.

3. Concluding remarks and outlooks

The number of works devoted to the study of liquid-phase selective oxidation of alcohols using silver-based catalysts is quite lower than those on catalysts based on noble metals, and especially on gold. This is probably because, at the low temperatures used for liquid phase

processes, they show a lower activity when compared to their homologues based on gold nanoparticles. Despite this, it is obvious that these systems are promising in such processes, since they could replace existing expensive catalysts based on platinum group metals and gold, provided their intrinsic activity and catalytic performance are increased up to a competitive level. Besides, the selectivity features of Ag-based catalysts are different of those of their Au-based homologues under equal reactions conditions. Silver catalysts are more selective to aldehyde formation [82], and may catalyze the oxidative cleavage of products during polyols oxidation [79,80], thus opening ways to new ranges of products.

But many issues related to the influence of various synthesis parameters (preparation method of catalysts, pre-treatment conditions, nature of support and modifier, active component content) and operation conditions (nature and concentration of alcohol, solvent and oxidant, substrate/catalyst ratio, reaction temperature, etc.) to optimize activity, selectivity and stability of Ag-based catalysts are either partially investigated or not studied at all.

Two other aspects of Ag catalysts have received little attention in relation to their use in liquid phase oxidation: its interaction with oxygen and the effect of particle size at the nano scale. At a variance of gold that does not even adsorb oxygen [88], the catalytic oxidative power of Ag is due to its ability to chemisorb oxygen in atomic form. The atomic oxygen could fit into the octahedral holes of Ag and cause the accumulation of oxygen within the bulk of silver [89]. Oxidized surface Ag species on the metallic Ag were inferred to be the active Ag species for the gas-phase partial oxidation of benzyl alcohol [67].

Concerning the effect of particle size, the investigation of oxidized Ag nanoparticles [90] has shown that the chemical bonding of oxygen species stabilized on small particles differs from the oxygen species adsorbed on bulk silver surfaces (monocrystals, foils and large particles), that are usually involved in gas-phase oxidation applications. The low charged oxygen with molecular type of bonding stabilizes on NPs of size $\leq 5\,nm$. Increasing particle size leads to the dissociation of O_2 species and the formation of strongly charged oxygen composed of oxide nanoparticles like Ag_2O or AgO type. The presence of extended defects in the microdomain large NPs facilitates the formation of Ag_2O or AgO layers covering metallic nanosilver [90]. Thus, one may expect that the catalytic oxidation properties of nano Ag-based catalysts can be very different depending on the particle sizes. This points to their commonality with Pd-based [12] and Pt-based catalysts [16], which surface oxidation properties are linked to the metal dispersion, and hence to the metal particle size.

In addition, development of highly efficient catalysts with desired properties is impossible without understanding of patterns of formation and stabilization of active catalyst sites. Molecular design of heterogeneous catalysts and understanding of principles of their functioning as a single complex system are key areas of current research in the field of catalysis. In this context, the questions of targeted selection of support, modifying additives, synthesis method and pre-treatment conditions, which ensure the formation of most active metal states on support surface and stabilize them during the catalytic process and storage, are very important and urgent. However, only in some of studies discussed above [71,75,79–83] attempts were made to identify the nature of active site. This remains matter of controversy: while some authors suggest that the active sites are metallic silver particles of different sizes, other researchers prove the activity of different types of ionic sites. One reason for this controversy may be the different nature of the oxygen species depending on the NPs size discussed above and also their dynamic equilibrium with the oxidant molecules. This dynamic character requires the use of sophisticated in situ characterization techniques (XAFS, high pressure XPS, DRIFTS) that have been applied to study related catalytic systems [10,16,91]. The full understanding of the nature of the *working* active sites of the Ag-based catalysts will require the use of such techniques as well as quantum-chemical modeling studies of both, the structure of the active site and its interaction with the substrate.

Thus, many issues related to the development of efficient and stable silver-based catalyst systems for liquid-phase oxidation of alcohols require further in-depth study, in particular, those related to selection of optimal catalyst synthesis method, study of the effect of particle size at the nano scale, and fine control of the metal-support interactions. The expected advances in these areas will contribute undoubtedly to approach the practical implementation of silver catalysts for selective oxidation of alcohols in liquid phase.

Acknowledgements

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