Green Chemistry

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Cite this: DOI: 10.1039/c0xx00000x

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TUTORIAL REVIEW

Deactivation of solid catalysts in liquid media: The case of leaching of active sites in biomass conversion reactions

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

This review is aimed to be a brief tutorial covering the deactivation of solid catalysts in liquid phase, with specific focus on the leaching case, which can be especially helpful to researchers not familiarized with catalytic processes in liquid phase. Leaching refers to the loss of active species from the solid that are transferred into the liquid medium, causing eventually a deactivation of the catalyst. Intriguingly, not many published studies deal with leaching, since this is a specific phenomenon in liquid phase and heterogeneous catalysis is mainly carried out in gaseous phase. However, as a consequence of the development of new processes for biorefieneries, an increasing number of reactions deal with liquid media, and thus, the stability and reusability of solid catalyst in this situation represents a huge challenge that requires specific attention. Leaching of active phases is particularly problematic because of its irreversibility and it can be one of the main causes of catalyst deactivation in liquid media, threatening the sustainability of the process. This tutorial review presents a survey of the main aspects concerning the deactivation due to leaching of active species from the solid catalyst: mechanisms, detection methods, impact of these factors on the global activity and finally, some procedures to try to minimize the leaching or to cope with it. A decision flowchart is presented to help in the study of the catalyst stability and reusability. Interesting biomass conversion reactions have been chosen as examples to illustrate the importance of these aspects.

1. Introduction

As a consequence of the shifting towards renewable feedstock to replace fossil fuels, new catalytic processes are being developed in which the utilization of solid catalysts is preferred. The heterogeneous catalytic processes present the advantage of the easy recovery of the catalyst and the reduction of the waste effluents. Besides, an increasing number of catalytic reactions in biorefining are nowadays being carried out in liquid media.[1]

Biomass feedstocks have in general low thermal stability, and therefore they are difficult to process in gas phase.[2] Water is the

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preferred option for a solvent,[3] but organic polar solvents[4] as well as ionic liquids[5-7] have been employed in a great number of recent research studies. Some examples of these liquid-phase reactions can be found in the catalytic transformation of lignocellulosic biomass to chemicals and fuels,[8-10] including the hydrolysis of cellulose,[11, 12] dehydration of carbohydrates[13, 14] and the subsequent transformation of the platform molecules to value-added chemicals and fuels[15, 16] or lignin depolymerization.[17, 18] Also, the transesterification reaction of vegetable oils to produce biodiesel (fatty acid methyl esters, FAME) is carried out in the presence of very polar methanol,[19] and the valorization of the sub-product glycerol proceeds in liquid medium.[20] Finally, the aqueous phase reforming (APR) of biomass-derived hydrocarbons in water is another example of liquid-phase reactions in the context of biorefineries.[21]

The utilization of a liquid medium in a heterogeneously catalyzed reaction can affect the catalyst stability negatively. One of the key factors when developing an industrial process is the stability of the catalyst. In this sense, the economic and environmental sustainability of the process depends on the possibility of reusing the catalyst. The usual high price of the components needed for the synthesis of a given catalyst makes the stability of the catalyst an essential requirement for any feasible industrial application. For instance, according to the techno-economic analysis of the industrial production of dimethylfuran (DMF) carried out by Dumesic and co-workers,[22] the catalyst cost is approximately a third of the total installed equipment cost. This is a good example of a prospect reaction within the field of biorefineries using organic solvents.[23]

The catalyst stability and deactivation in gas-solid catalytic reactions have been extensively studied and established in the past years. Numerous reviews, proceedings and investigations address the mechanisms of catalyst deactivation when gas reactants are used and the possibilities of regeneration or prevention of the deactivation.[24, 25] However, much less attention has been paid to understand the deactivation processes in liquid media, probably due to the fact that most of the industrial catalytic processes are carried out in gas phase. Initial studies covered the stability of supported metal catalysts in liquid phase, mostly in oxidation reactions.[26-28] Recently, this problem has been adressed in the developement of new liquid processes in biorefineries.[2, 29-31] The number of scientific articles related to catalysis in liquid phase has increased significantly and so, a tutorial review of the main types of deactivation of catalysts field appears to be of interest, especially for those not familiarized with the handling of catalyst in liquid phase reaction.

One of the crucial aspects regarding the deactivation of catalyst in liquid media is the possibility of leaching components of the catalyst into the liquid medium. This aspect includes the understanding of the mechanism by which the process takes place, its impact in the deactivation and the catalytic activity, and finally the possibilities of minimizing and/or eliminating this phenomenon. An assessment of these issues will thus be the main objective of this tutorial review. Although other deactivation mechanisms will be discussed, the main focus of this review will cover the deactivation of catalyst by leaching.

Leaching has economic consequences, especially for expensive catalysts, and presents very relevant environmental implications. The sustainability of a catalytic process can be threatened by the presence of chemical species in the effluents. Many solid catalysts contain metal species that can be very toxic. Although the extent of leaching represents usually only ppm traces of metal cations in the effluent and implicates a low impact in the deactivation, the high toxicity of the leached metal species would require additional purification steps to clean the effluents. This complicates the process and has a negative impact on its cost.

The present review shows some examples of deactivation of catalysts studied in literature related to biomass conversion reactions. Nonetheless, the aim is not to make a thorough study of all the published work within this field, but to offer the reader the main guidelines and some representative and illustrative examples. Finally, although this tutorial review is mainly focused on reactions related to processes in biorefineries, it has a wider scope and is of general interest to other areas dealing with organic reactions conducted in liquid medium and catalyzed by solids, for instance, in the synthesis of pharmaceuticals and other fine chemicals.

2. Overview of mechanisms of catalyst deactivation

The process of catalyst deactivation has been widely described in

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the case of gas-phase reactions. Excellent reviews are reported elsewhere.[24, 25] Following Bartolomew, there are basically five types of mechanisms of catalyst deactivation in gas-phase that are compiled in Table 1. These five types can be grouped, based on the nature of the mechanism into three categories: physical, thermal and chemical.[25, 32] Despite this classification it is not always easy to identify separately the mechanisms causing the catalyst to lose activity. In most of the cases, the deactivation is the result of more than one cause, even having the same effect. The deactivation causes that can take place in liquid medium are similar to those reported in gas phase, although the specific mechanisms differ slightly, as well as their relative relevance.

The first deactivation cause, fouling, involves the deposition of chemicals present in the reaction medium on the surface of the catalyst. The origin of these species is diverse: reactants, principal products or by-products and even impurities can be physically deposited for a number of reasons, including heavy weight, insolubility in the reaction medium, steric effects, adsorption, etc. A special fouling case is for reactions in which the products possess larger size than the reactants. The product molecule, once formed, can in this case be occluded in the porous network of the solid. Whichever the reason is, the final result is that reactants do not have an easy access, or access at all, to the active sites. There are a number of examples reported in the literature where fouling has occurred. For example, in the synthesis of biodiesel catalyzed with organosulfonic acid functionalized silica, catalyst deactivation was found as result of site blockage by adsorbed intermediates or by-products, i.e, fouling.[33] In gas phase this mechanism is mainly known as coking. Coke refers to heavy hydrocarbons generally produced as a result of the a combination of several reactions such as dehydration, dehydrogenation, isomerization, aromatization, oligomerization and/or condensations of molecules present in the reaction medium (reactants, products, impurities or by-products) on the surface of the catalyst.[24] This can also occur in liquid phase. Coke formation has been detected in Ni-Co supported catalyst in glycerol reforming to obtain hydrogen.[34]

The second mechanism of deactivation is also physical in nature, and is caused by mechanical alterations of the solid catalyst. The main phenomenon in liquid medium is the attrition, causing the size reduction and/or the breakup of the catalyst particles.[24] This can be especially problematic when recovering the catalyst. Formation of fine particles too small to be retained or separated can make the reutilization of the catalyst difficult, especially in fluid or slurry beds. When operating in continuous mode the formation of smaller particles can result in clogging and in the subsequent build-up of overpressure in the reactor.

The third type of deactivation is sintering; the thermodynamically driven growth of crystal size. The effects are loss of surface area or even collapse of the porous structure. The diffusion of surface cations or atoms is facilitated by the temperature and as a result, the size of the crystallite of the catalytic component becomes larger. In presence of water, hydrothermal conditions can be specially threatening. The sintering results unavoidably in a loss of the number of active sites exposed to the reaction medium. Sintering of dispersed metals has been described in aqueous medium.[35] For example, the sintering of Pt supported over silica-alumina catalysts occurs faster in liquid water than in wet air,[36] and the structural stability of different zeolites decreases significantly in water medium, which needs to be considered carefully in typical biomass conversion processes.[37] In some cases, the sintering can be avoided by adding promoters that ensure the dispersion of the active metal.[34] Some of these thermal degradation processes can appear simultaneously. For example, high pressure and temperatures used in glycerol hydrogenolysis caused the collapse of the porous network and sintering of the Cu metal particles in a silica-supported copper catalyst.[38]

Apart from the aforementioned physical and thermal mechanisms, deactivation driven by chemical mechanisms can also take place. Poisoning refers to the chemisorption of species that impede the proper functioning of the active site. Traditionally, poisoning has been described as chemisorption of certain substances over metallic particles, but other examples can refer to ion exchange processes. Sulfonic acid functionalized catalyst or acid sites in general can potentially be deactivated by ion exchange of the protons with metals present in the medium. This behavior has been found in ion exchange resins employed in the esterification of bio-oils, where the main cause of deactivation was ion exchange with metal ions.[39] Therefore, the presence of impurities in the initial feedstock can potentially deactivate the catalyst. In the esterification and transesterification of oils with sulfonated carbons and silicas as catalysts, the active site is deactivated just after contact with the alcohol. This is explained by the reaction to form sulfonate esters.[40, 41]

The fifth deactivation case refers to chemical and structural alterations of the catalyst. It is also chemical in nature, but while the poisoning is an interfacial phenomenon, this mechanism involves the formation of new solid phases. The new phases can be formed through the reaction of some of the catalyst components with any chemical present in the reaction medium (reactant, product, by-product or impurity) or any other components of the catalyst. Another possibility is a phase change driven by the reaction conditions (temperature, pressure, solvents, etc). Some of the most common deactivation processes gathered in this mechanism include phase transitions by reaction with the solvent,[37, 42] and dealumination or hydrolysis in the case of zeolites, although this can also be considered as leaching.[37] Another typical example of formation of new phases is the oxidation of metals by the solvent (water) or oxygen present in the reaction to form catalytic inactive oxides. This has been described in the liquid phase conversion of glycerol with metallic catalysts.[43] Some authors have even proposed a kinetic model for the mechanism of catalyst deactivation via over-oxidation with oxygen. This is the case in some reactions of oxidation of alcohols in liquid medium.[44, 45] Occasionally, a change of phase of the support during the reaction can have a beneficial effect, as in the case of alumina-supported Pt catalyst in APR of glycerol. Here, the initial alumina forms bohemite, which is active in the reaction of dehydration of glycerol.[46] When compared to the deactivation mechanism in gas phase, the chemical alterations in liquid media are more plausible, since the reaction with the solvent is favored to a much greater extent.

Finally, the last deactivation mechanism collected in Table 1 is the lixiviation or leaching of active phases. It is specific for reactions in liquid media and has to do with the solubilization or dissolution of components of the catalyst into the reaction medium. The IUPAC defines it as an extraction procedure, comprising the dissolution of material from a solid phase with a liquid in which it is not wholly soluble. Strictly speaking, it may be included in the previous category, as it in many cases implies the formation of a new phase that become soluble in the reaction medium. However, in this specific case, the new phase is solubilized into the liquid. It has its counterpart in the gas-phase systems but in this case the phases are volatilized and consequently removed in the gas flow. In batch liquid reactions, the leached species stay in the reaction medium and may play a catalytic role as active species. The problem of the stability of solids in water has attracted attention in many studies. Sheldon and coworkers studied the case of leaching of various metals in different liquid phase oxidation reactions which they pointed out, are particularly challenging.[26, 47] In 2002, Okuhara published a complete review about different water-tolerant solid acid catalysts.[48] In most of the reported cases, the cause for the deactivation of solid catalysts in liquid media is the partial solubility of the active species in water, i.e. leaching. The support of the catalyst can also be affected during reaction and it can be dissolved in the reaction medium. This happened, for example, when using TS-1 zeolite for ammoxidation reactions. The presence of basic ammonia dissolved the silica, and the framework Ti was transferred and precipitated as TiO_2 on the surface of the zeolite.[49]

The growing importance of the leaching phenomenon in catalytic reactions can be perceived by the evolution of scientific documents published in this particular area, as shown by the data in Figure 1. Three representative keywords were selected (leaching, catalyst and biomass), but other keywords could be incorporated to the search with the same final conclusion. Even though not all the reported search hits are relevant, it is obvious that the problem of leaching in catalytic conversion of biomass is becoming more visible. Due to its relevance and its peculiar nature and also because of its impact in the environmental sustainability of a given chemical process, it deserves a deeper explanation in this review. Next sections will discuss aspects such as the description of the chemistry behind the leaching of catalytic species, the detection of the leaching phenomena, the determination of the impact in the deactivation, the role of the leached species in the catalytic activity and finally, different manners to prevent or to deal with the leaching.

Table 1 Causes of catalyst deactivation.[25, 32]

Entry	Nature	Type	Mechanism	Description
1	Physical	Fouling/coking	Lack of accessibility	Physical deposition of chemical species by deposition (fouling).
2	Physical	Mechanical alterations	Loss of active phase or pressure build up	Crushing, attrition, abrasion, erosion of the catalyst particles.
3	Thermal	Sintering	Decrease of the number of exposed active sites	Loss of surface area or collapse of the porous network by growth of the crystal size driven by thermal effects.
4	Chemical	Poisoning	Decline of intrinsic activity	Chemisorption of species on catalytic sites.
5	Chemical	Formation of new inactive phases	New phases are not as active	Reactions affecting the components of the catalyst leading to different phases (hydrolysis, hydration, oxidation, etc.)
6	Chemical	Leaching	Loss of active sites	Dissolution of one or more active components into the reaction medium.

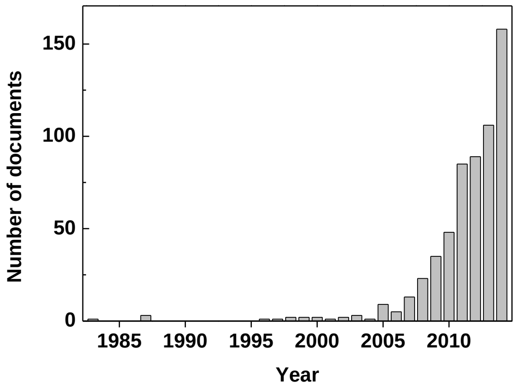

Fig. 1 Evolution of the number of scientific documents published per year using the search term: "leaching" (in all fields), "catalyst" and "biomass" excluding "bioleaching". Source: Scopus

3. Mechanisms of deactivation by leaching

It is possibly to identify several deactivation mechanisms caused by leaching, which is relevant when using bulk catalysts, supported catalysts (both support and active phase) as well as mixed-phase catalysts.

- *Direct solubilization in the liquid medium.* Most of the metal oxides, hydroxides and carbonates frequently present in catalysts can be slightly soluble in water.[48] Even if the extent of the leaching is very low, this can have influence on the catalytic behavior and deactivation. When mixed oxides are used, one can have a selective leaching of one of the components. For instance, hydrotalcites in water selectively dissolve Mg.[50]
- *Chemical transformations.* The solvent, or some acids or bases present in the medium can react with components of the solid catalyst forming soluble species that are subsequently dissolved. In the presence of water, some oxides can form the corresponding hydroxide, with increased solubility.[42] In the

case of oxidation reactions with immobilized metals, leaching is generally due to the solvolysis of the metal-oxygen bonds, through which the active site is attached to the support.[26] Leaching is particularly increased in the case of oxometal species (e.g. vanadyl, chromyl, molybdenyl).[26] When zeolites are used in acidic medium, it is common to have hydrolysis of Si-O-Al bonds and form extra-framework octahedral Al species that are easily leached out.[37, 51] Leaching by chemical transformation is very common when using sulfuric, nitric or hydrochloric acid with metal oxides that can form soluble salts. Basic conditions can also facilitate leaching. This procedure is habitually used in order to recover metals from spent catalyst.[52] A modification of this leaching mechanism is when chelating agents are present, like carboxylic acids, polyhydroxy compounds and other organic compounds containing other oxygen, nitrogen or sulfur functionalities. These compounds form complexes with the components of the catalyst, typically metals, and have very effective extraction abilities.[52]

In brief, leaching of different species depends on several factors in the reaction medium: pH, oxidation potential, presence of chelating species, temperature and the presence of ions.[27] Sometimes the reaction conditions can be modified to improve the catalyst stability as it will be explained later, but it is imperative to determine if leaching is taking place, so its impact is minimized.

4. Detection of the leaching process and activity of leached species

The detection of the phenomenon of leaching or lixiviation is essential to fully understand the deactivation process. There are several ways of accomplishing this task as compiled in Table 2.

The first approach consists of chemical analysis of the reaction liquid to identify the presence of soluble species. Different factors can have a substantial impact on this determination and therefore have to be taken into account. The sampling of the reaction liquid is extremely important. Preferably, the sample has to be taken directly from the reaction medium under relevant reaction conditions.[28] When this is not feasible, other methodologies can be applied, for instance, hot-filtration or centrifugation. It needs to be commented that the modification of the temperature can affect the solubility of chemical species, so it is possible that leached species can precipitate at the sampling temperature and leaching phenomena is misinterpreted in the subsequent analysis. It has even been reported that soluble species are the active species, but re-deposition on the support takes place after completion of the reaction and returning to room temperature. This is the case of for instance Pd-catalyzed coupling reactions where metal species in solution are the real active species.[53] Controlling the atmosphere can also be important if the species is expected to be sensitive to the presence of oxygen, moisture, CO_2, etc. and to precipitate before completing the analysis. The development of procedures for in-situ determination of leaching might be preferable. In line with this, Granados and coworkers developed an in-situ method to indirectly estimate the amount of leaching in the case of transesterification of triglycerides to produce biodiesel with CaO by using conductivity measurements.[54]

Table 2 Detection of leaching in the catalyst.

Approach	Measurements	Remarks
Chemical analysis of the liquid	Sampling of the reaction liquid and chemical analysis	Sampling needs to be representative of the real reaction situation. Analysis methods need to be sensitive enough.
Activity of the soluble species	Contacting the catalyst with the reaction medium, and activity measurement of the soluble species	The leached species do not necessarily have to be active.
Characterization of the used solid	Chemical, structural and textural analyses	Information is provided about different deactivation mechanisms, but presence of leaching might be missed if lixiviation is limited.

Another important factor to take into account is that the detection limit of the analytical techniques employed has to be very low to provide significant results. This is of special importance when determining the leaching extent of supported catalyst, in which the initial loading of the studied element is very low. Especially when working with low amounts of catalyst, it can happen that leached species cannot be detected, even though they can represent a high percentage of the initial active sites. Different analysis processes can be used for elemental analysis, being the most common atomic spectroscopy and mass spectrometry coupled with inductively coupled plasma (ICP-AES and ICP-MS), X-ray fluorescence or X-ray photoelectron spectroscopy. The detection limit of these techniques will depend on the element and the sample composition, so it is important to choose the most appropriate for a given application. As an example, in the conversion of cellobiose to sorbitol, Ru/C catalyst was used in low amount (0.0375 g in 25 g of solvent), with a low Ru loading (3.6 wt%).[55] The detection limit of the analytical method employed was 2 ppm (ICP-AES), which corresponds to almost 4% of the initial amount of Ru present. This means that even if 4% of the Ru was lost in the reaction it could not be detected. Accordingly, it will be difficult to clearly identify the presence of leaching just by analyzing the reaction liquid.

The second approach to detect leaching is based on the indirect determination of the presence of active soluble species in the reaction medium by testing the catalytic activity of the soluble species. This can be accomplished by separating the catalyst from the reaction medium after a certain time, and continuing the reaction without catalyst under the same reaction conditions. Addition of fresh reactants may be useful. An alternative is to contact the catalyst with only the reaction solvent(s) (without the reactant) under the reaction conditions for a desired time, then separating the solid, and starting the reaction with the liquid phase after addition of the fresh reactant.[56] This latter approach presents the advantage of a more controlled situation, since other deactivation phenomena, such as deposition of carbonaceous species, are avoided. Carbon deposits can potentially block the access to the active sites and protect them from leaching. However, some of the chemical compounds present in the real reaction can also have a big impact on the leaching. For example, the formation of acid products can decrease the pH and promote the leaching. Both experiments should thus be done and compared to get extra information and a deeper understanding of the system.

Even very small amounts of solubilized species can represent a large fraction of the overall catalytic activity, leading to a false conclusion on the leaching phenomenon and its impact in the catalyst activity.[26, 57] Three situations can be found here. In the first case, all the activity is due to leached species. This was the case in the dehydration of xylose to furfural with vanadium phosphate oxides in water-toluene media, where a few hundreds of ppm of V and P were verified to lead to the same activity results as the total solid catalyst.[57] The performance observed during the reutilization of the solid was due to the homogeneous active V and P species provided by the leaching of these species into the solution in each run. If this effect is not identified, wrong conclusions about recyclability and stability of the catalyst can be inferred. In the second case, the leached species can have some extent of contribution to the total activity, or even some kind of synergetic effect. An example where such synergy effect was identified is biodiesel production with CsF/Al_2O_3 catalyst, where the presence of both alumina and dissolved CsF seemed absolutely necessary to observe any conversion.[58] Finally, it is important to bear in mind that in other cases, the presence of soluble species has not shown any impact on the activity. For example, this occurred in the oxidation of 5-hydroxymethylfurfural (HMF) in ionic liquids with supported Ru catalysts. Here only the heterogeneous species on the surface of the catalyst presented activity.[59]

The extent of the homogeneous catalysis is not always easy to estimate, as it can vary with the progression of the reaction. This is illustrated in several reports on biodiesel production with CaO catalyst, where the contribution of the soluble species has been evaluated. Here different phases were formed as reaction progressed, changing the leaching phenomena as the solubility of these new species in the reaction medium was different.[54, 60] In the case of acidic zeolites for fructose dehydration, some authors speculate that primary active species are small zeolite fragments or oligomers containing octahedral or extra-framework aluminum.[61]

Finally - and additional to the previous experiments - a thorough analysis of the used catalyst is important for revealing leaching. It is important to stress that all the measurements directed to detect the leaching should be carried out. If the loss of active species is small and only the spent catalyst is analyzed, the detection of leaching may be missed. This is why all the approaches are complementary and equally important. Besides, the analysis of the solid is essential for uncovering other causes of deactivation, such as coke formation or sintering.

5. Leaching and deactivation

While some of the deactivation processes showed in Table 1 can be reverted, it is very difficult to regenerate a catalyst after leaching. For example, in the case of sugar dehydration to furfural, a deactivation by coke deposition is usually easily solved by calcination of the solid deposits.[62] However, when the active site of the catalyst is leached, there is a clear loss of active sites and consequently of activity in successive cycles.[56] This is why the study of the leaching is so important in liquid phase reactions.

Recently, an increasing number of papers have addressed the problem of catalyst deactivation by leaching of active species to the reaction medium in the field of biorefineries (Figure 1). Most of these studies are related to biodiesel production, probably due to the fact that it is one of the most established biorefinery-related reactions. In a recent review on inorganic heterogeneous catalysts for biodiesel production, leaching of active phase was identified as one of the major problems limiting stable performance of the catalyst.[63] The presence of highly polar methanol at relatively high temperatures made the lixiviation process quite favorable. Many of the acidic catalysts studied were based on solids with sulfur-based functionalities. In particular, the lixiviation of sulfonic acid groups in the solid catalysts was identified as the main cause of the deactivation in several esterification and transesterification reactions with different catalysts, e.g. sulfonated zirconia,[64, 65] organo sulfonated silica[33] and sulfonated carbons.[66] In other acidic catalysts, like supported heteropolyacids, leaching of active phase has been found to occur under reaction conditions.[67]

Lixiviation leading to catalyst deactivation has also been detected when basic catalysts have been employed in the transesterification reaction. Alkali and alkali-earth oxides, like CaO or hydrotalcites, present leaching problems under biodiesel synthesis conditions.[54, 68, 69] Although some studies report the prevention of the lixiviation by stabilization of the active phase over supports,[70] other authors have detected leaching in several studies with supported alkalis and metal oxides.[71-80]

Several examples of leaching are also found in other interesting biorefinery-related reactions in liquid phase. This is the case of the hydrogenation of levulinic acid to γ-valerolactone, where leaching of supported metals was detected using Ru-Sn/C[81] and Cu/ZrO_2.[82] This was also the case with sufonated amorphous carbon catalyst used in the hydrothermal conversion of cellulose to lactic acid. After the first reaction cycle, 40% of the initial sulfonic groups leached from the catalyst.[83] In the hydrogenolysis of cellulose to polyols, deactivation by leaching of the supported Ni and W over silica-alumina was again observed.[84] Also, in the hydrogenolysis reaction of tetrahydrofurfuryl alcohol to 1,5-pentanediol over $Ir\text{-}Mo/SiO_2$ catalyst it was found, that Mo leached into the reaction (Ir remained stable) causing a loss of activity with time on stream.[85] Other authors have reported some leaching from metal oxides and functionalized zeolite catalysts in the aldol condensation of furfural and acetone to form larger molecules that can lead to alkanes.[42, 86-88] In the conversion of lignocellulosic biomass via pyrolysis, metal lixiviation was identified as one of the causes for catalyst deactivation when Ni and Cu were supported over γ-alumina.[89] De Vlieger et al. reported the deactivation of Pt and Pt-Ni supported catalyst in APR of ethylene glycol. The proposed mechanism included the leaching and re-deposition of the alumina phase support, causing a loss of exposed area of the metal active sites.[90]

Even though this list may seem discouraging, there are also examples where leaching of catalysts in biomass conversion reactions has not been observed or conditions for negligible leaching have been found.[91-94]

Leaching is obviously an economic problem as it reduces the life of - very frequently expensive - catalysts. But the leaching conveys other very important environmental and economic concerns; presence of toxic chemical compounds downstream the process. These substances, in some cases heavy metals, must be removed from the streams while being handled under appropriate and costly protocols to prevent spills in the environment. Eluted species may also have a poisoning effect on downstream catalysts. For example, the presence of Fe or Cu in the reaction medium arising from the leaching of the reaction vessel reduced the activity of rhodium catalyst in hydrogenolysis of glycerol.[95]

6. Coping with the leaching

As seen in the previous examples, there are many cases in which irreversible catalyst deactivation by leaching is a challenge in a great number of the reactions carried out in liquid phase. Different procedures can be used in order to prevent or minimize the leaching of the catalyst as summarized in Table 3. The first approach consists of modification of the reaction conditions. Different factors affect the extent of leaching, as commented in section 3. First, the solvent significantly affects the behavior of solid catalysts towards leaching. Changing the polarity of the medium is thus one of the easiest options to try to avoid leaching. Diverse examples of this behavior in biorefinery related reactions have been found in literature.

Changing the solvent from water to methanol avoided the lixiviation of metals in the hydrogenation of levulinic acid.[82] When recycling mesoporous silica-supported 12-tungstophosphoric acid catalysts in the dehydration of xylose to furfural, Valente and coworkers found that the loss of activity in successive runs was significantly lower in DMSO than in water/toluene.[56] There is also the case of similar materials used in different reactions with very different deactivation profiles. For instance, supported Ru-hydroxide catalysts have been reported to be stable towards leaching in some reactions carried out in non-polar organic solvents, as the oxidation of monoterpenic alcohols in toluene.[96] In contrast, lixiviation of Ru species was detected in the liquid after oxidation of HMF with a similar supported catalyst when ionic liquids were used as solvent. Even though Ru-hydroxide is insoluble in most solvents, such as toluene, the polar ionic liquid was apparently able to dissolve some of the active sites. In this latter case, the soluble species were not active in the reaction.[97] This is a clear example of how important the selection of the reaction medium is when trying to minimize the leaching phenomena. If possible, a solvent were the solubility of the catalysts or active species is negligible should be selected.

High pressures can be detrimental for the leaching properties of catalysts. When using a zeolite supported vanadia catalyst in the oxidation of HMF no leaching was detected at atmospheric pressure, while higher extent of leaching was found at higher pressures.[98] This is a good indication that the parameters of the reaction have a great impact on the stability of the catalyst.

Table 3 Possible procedures for the prevention of the leaching.

Type	Change in	Brief explanation	Refs.
Reaction conditions	Solvent	Polar solvents are usually more aggressive	56, 82, 97
	Pressure	Higher pressures can affect the stability	98
	Temperature	Higher temperatures (hydrothermal conditions) are usually detrimental	99
	pH	High or low pH can promote the solubility	36, 100
Catalyst	Alternative materials	When possible, use other components (metals, supports, etc.)	98, 101
	Pretreatment	Different conditions in the pretreatment modify the subsequent catalyst	92, 102, 103
	Washing	Adding a washing conditioning step in the synthesis of the catalyst can help to obtain a stable material	104-106
	Modifications of the surface	Metal catalyst can be stabilized towards leaching by Atomic Layer Deposition	107
Reaction type	Gas phase	Gas phase reactions can diminish problems due to leaching	

Hydrothermal environments may be especially critical for the stability of catalysts. Under such conditions, polyoxometalates have been found to leach when utilized in the conversion of cellobiose to gluconic acid.[99] Other conditions, such as the application of ultrasound, can also increase the leaching.[108] The pH of the medium also affects the solubility of the material. This is of special importance when reactants, products or by-products have acidic or basic properties. Vilcocq et al. reported an increased deactivation of a Pt/Al_2O_3 catalyst when formic acid was produced as by-product in sorbitol transformation to alkanes.[36] In a different example, leaching of Ni catalyst in APR of biomass was prevented by changing to alkaline conditions.[100] Finally, some of the species present in the reaction can aggravate the extent of leaching by reacting with the catalyst. This is the case in transesterification of oils with high acid content using solid basic catalysts. The free fatty acids react with the base to form soaps, causing a deactivation by leaching, among other problems.

The leaching can secondly be reduced by modifying the catalyst. The type of supported metal also determines the extent of leaching. In the catalytic hydrodeoxygenation (HDO) of vegetable oils to form alkanes, molybdenum carbide exhibited better resistance to leaching than noble metals.[101] Similarly, the used support can also play an important role on the stability of the final catalyst.[98] Alternative options consist of carrying out some pretreatment procedures on the catalyst. Dumesic and coworkers found that increasing the temperature of the catalyst reduction treatment affected the leaching of Re into the solution in the hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran.[102] The reason for this observation was, that some rhenium oxide phases are soluble in water, so controlling this aspect is crucial to avoid the solubilization of the catalyst in aqueous reaction environments. In this sense, pre-reduction of oxidized catalysts may suppress the dissolution of metal species by forming lower-valent or zero-valent metal oxides that, in some cases, are less soluble. The preparation method also plays an important role. While mixed Mg-Al oxides prepared by co-precipitation were found to be unstable in water medium,[109] a similar synthesis involving hydrothermal microwave treatment and an activation step with $Ca(OH)_2$ showed low leaching and better stability.[103] Other modifications of the catalyst can involve the addition of promoters. For example, the addition of Pt improved the stability of mixed Mg-Zr oxide catalysts in furfural valorization with acetone.[110] The temperatures of the pretreatment and the nature of the organic acid sites can likewise affect the stability, as reported in the dehydration of xylose with arenesulfonic SBA-15 catalysts.[92] Even a washing procedure or -treatment can be enough to eliminate species more prone to leaching from the surface of the catalyst, hence selecting the most stable ones, without affecting significantly the activity.[106] This happens naturally in successive reaction cycles. It has been frequently observed that the amount of lixiviated material decreases with the cycle number.[104, 105, 111] More recently, a very interesting methodology was published by the group of Dumesic.[107] This consisted on stabilization of a Cu catalyst by deposition of a thin layer of alumina by atomic layer deposition (ALD). The overcoat of alumina prevented sintering and leaching of the Cu particles during reaction, generating a catalyst that was more stable in the liquid phase hydrogenation of furfural.

Finally, if none of the compiled procedures in Table 3 works, it can be possible to run the reaction in gas phase. Nevertheless, the large polar molecules used in biorefinery-related reactions are usually nonvolatile and this solution is therefore not applicable.

7. Evaluation of the stability and recyclability of a catalyst

Figure 2 shows a decision flowchart that can help to evaluate and determine the stability and recyclability of a solid catalyst in liquid medium. First, experiments directed to the evaluation of the leaching of the catalyst should be carried out. If some catalyst leaching is detected, the next step should be the evaluation of the catalytic activity corresponding to these leached species (see Figure 2). As mentioned earlier, these two actions will confirm the existence of a leaching phenomenon. Characterization of the used catalyst can also indicate the presence of the leaching if, for instance, changes in composition or phases are detected. If leaching is detected, it is important to contemplate the necessity of modifying some of the reaction conditions to decrease or minimize the accompanying deactivation (Table 3).

The following step is the verification of the catalyst reusability - or in the case of flow reactions - the life time of the catalyst. When dealing with batch reactions, the most common way of testing this is to run consecutive reactions with the catalyst. It is important to note that in some cases when a single measurement is used in the test, the results can be misleading. The deactivation process can be shadowed depending on the conditions selected in the single measurements. If deactivation kinetics prevails as shown in Figure 3, it is clear that the activity measurements at different reaction times (1, 2 and 3) will give an altered picture of the deactivation process. While position 2 will clearly prove the presence of deactivation, running the experiment for longer times until position 3 will indicate the opposite, namely that the catalyst is stable. It is thus essential to conduct reuse tests at lower conversions than 100% to determine whether deactivation occurs or not.[112]

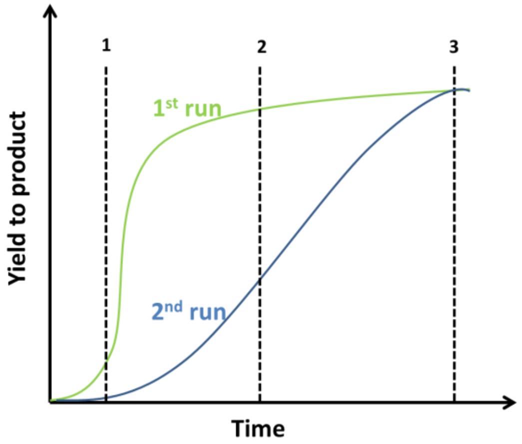

Fig. 3 Hypothetical kinetics showing the effect of sampling at three different reaction times on the detection of the deactivation of a catalyst during two consecutive catalytic cycles (1st and 2nd run).

When batch reactions are carried out, it must be stressed that the ability to recycle a catalyst includes other minor details, such as the effective recovery of the solid from the reaction medium and its consecutive reuse. This aspect is essentially important when handling small quantities of products. Losses of catalytic material are frequent during operations such as filtration, centrifugation, washing, etc. This has been the case in some studies, claiming that the lack of recyclability is due to the loss of catalytic material during the separation and recovery step.[92, 113] When handling basic solid catalysts, deactivation can occur due to the presence of atmospheric CO_2 which form carbonates. Oxidation and/or hydration of the active phases can also take place by contact with atmospheric air, leading to wrong conclusions on the deactivation and reutilization of the catalysts. The separation of the catalyst must be carried out under inert conditions to avoid these issues.[114] When continuous conditions are employed handling problems are avoided, although other difficulties can appear such as costly equipment and necessity of shaping the catalyst.

In some cases, the activity in the successive cycles increases despite the deactivation effect. This is due to the presence of induction periods in the reaction. This means, that the catalyst needs time to undergo a structural change (e.g. swelling in the case of polymers), that will favor the reaction rate and thus increase the conversion in subsequent catalytic cycles.[66]

When evaluating the reusability of a catalyst the characterization of the used catalyst is essential to understand the deactivation mechanisms, and to propose an adequate regeneration procedure. The study of the composition, crystalline phases, surface area and other properties will provide useful insights of the possible deactivation phenomena taking place during the reaction. The most common regeneration mechanism for fouling and/or poisoning is the thermal calcination treatment,

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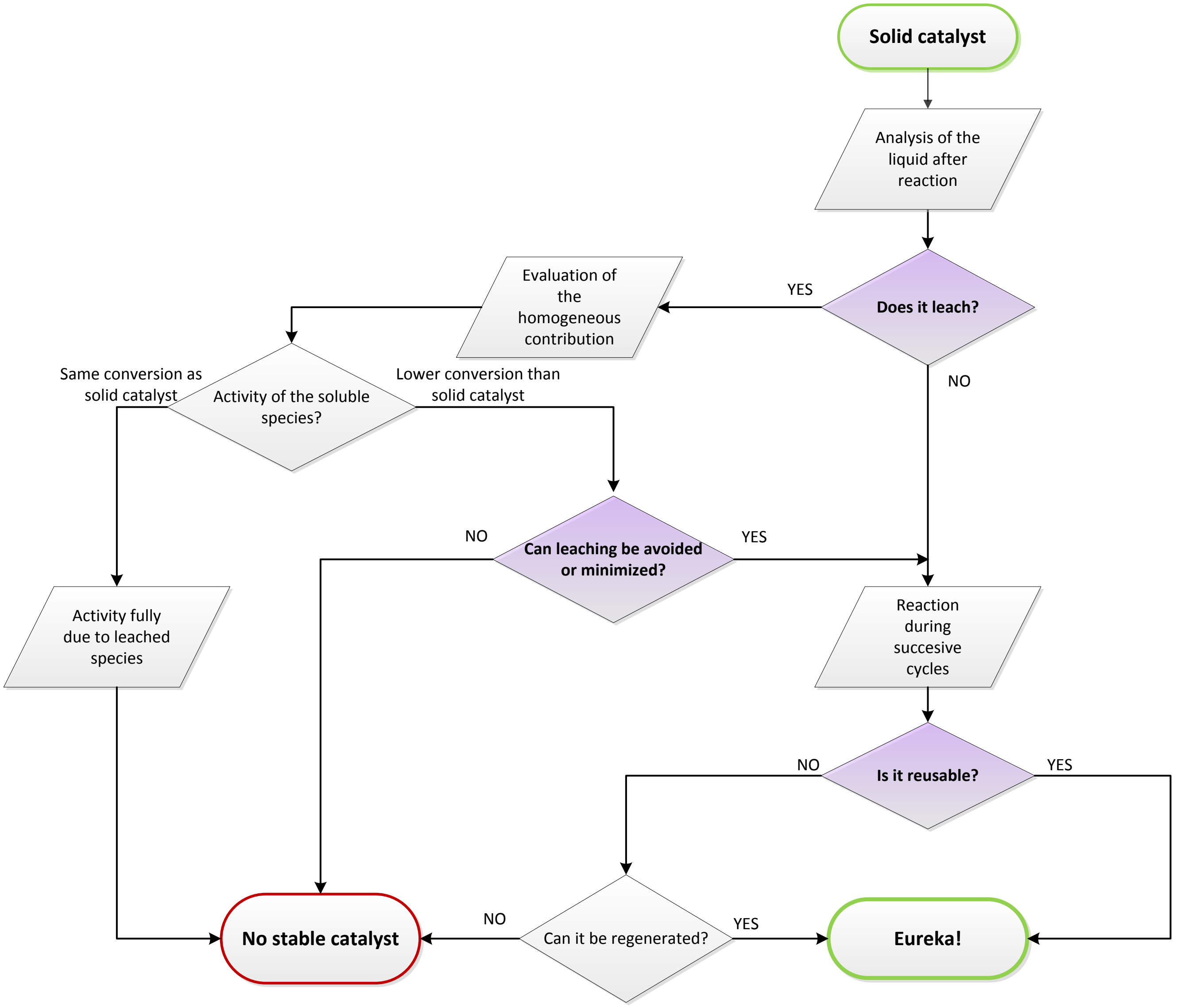

Fig.2 Decision flowchart to evaluate the stability and reusability of solid catalysts in liquid phase.

which will remove the deposited species. This type of treatment has been described in numerous scientific studies.[115-117] Note that the combustion of adsorbed coke species by thermal treatment may not be possible if the catalyst is not stable at the required temperature or is sensitive to oxidation. In the latter case gasification of the deposits can also be achieved with other milder oxidants agents like water or even with inert or reducing agents like N_2 and H_2. Obviously, removal of deposits or poisons present on the surface of the catalyst will not recover the initial activity if there is deactivation by leaching.[118] Other regeneration procedures include rinsing with solvents, acid or basic solutions, drying, or even chemical treatment aiming at removing the deposits and/or poisons to restituting the active sites, such as oxidizing the coke by H_2O_2.[119, 120]

8. General remarks

The main objective of this tutorial review is to draw the attention and give general guidelines regarding the phenomenon of the leaching of solid catalysts in liquid media, especially to those not familiarized with the utilization of solid catalysts in liquid processes. Leaching is very often underestimated and not properly evaluated. For example, in a recent study by Hájek et al. on production of biodiesel using K–based catalyst it was remarked, that not many previous studies even addressed the problem of leaching.[121] Omitting this crucial information in the discussion of the activity of the catalyst can lead to misleading conclusions and should be avoided.

Ideally, the extent of leaching should be negligible, but in most reactions performed in polar solvents and at high temperatures some leaching will always be present. However, this does not necessarily mean that the given catalyst cannot be utilized in any industrial process. Every reaction case will require a particular evaluation of the pros and cons of the use of the catalyst, together with a study of possible ways to design the catalytic process. The presence of leaching can have environmental consequences too. In the case of toxic elements, recovery of the leached species must be conducted to prevent downstream contamination. This implies the capture of the leached species by different methods to transfer them to a solid phase with the consequent concentration. In the case of expensive catalyst, the reconstitution or the extraction of the active catalytic species by different metallurgic procedures can be an interesting option to recycle the leached species in other applications, including as a catalyst. The lifetime of the catalyst needs to be taken into account when studying the feasibility of the industrial process, and the possibility of regeneration. Even though the presence of leaching will shorten the catalyst lifetime, an economical study will determine if the catalytic process is still viable. Finally, it has to be noted that in some contexts the leaching of expensive metals from used catalysts is a standard procedure in metal recovery processes, which enables the recycling of the metal from waste catalysts and represents a necessary step to minimize environmental impacts.

9. Conclusions

New questions arise when studying the stability of solid catalysts in liquid media compared to gas phase reactions; the solubility of the catalyst and the homogeneous contribution of the leached species. An increasing number of scientific articles in the context of green chemistry and biorefineries deals with reactions in liquid phase using solid catalysts, and not all of them account for the possible presence of leaching. It is imperative to remark that the reusability of the catalyst during several catalytic cycles by itself does not imply catalyst stability. If a homogeneous catalytic contribution is present, the total activity can be due to a small fraction of very active soluble species. This is why leaching tests and measurements of homogeneous catalytic contribution are indispensable to clearly rule out the deactivation by leaching.

This review is aimed as a road map to study the stability of solid catalysts in liquid media. The first step comprises the detection of the presence of leaching and the estimation of its importance. Second, some procedures have been given to try to minimize the extent of leaching. Finally, the reusability of the catalyst and the lifetime need to be addressed.

Acknowledgments

The authors would like to acknowledge funding and contributions from Centre for Catalysis and Sustainable Chemistry, DTU Chemistry, Institute of Catalysis and Petrochemistry, CSIC and Haldor Topsøe A/S to part of the reported work.

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