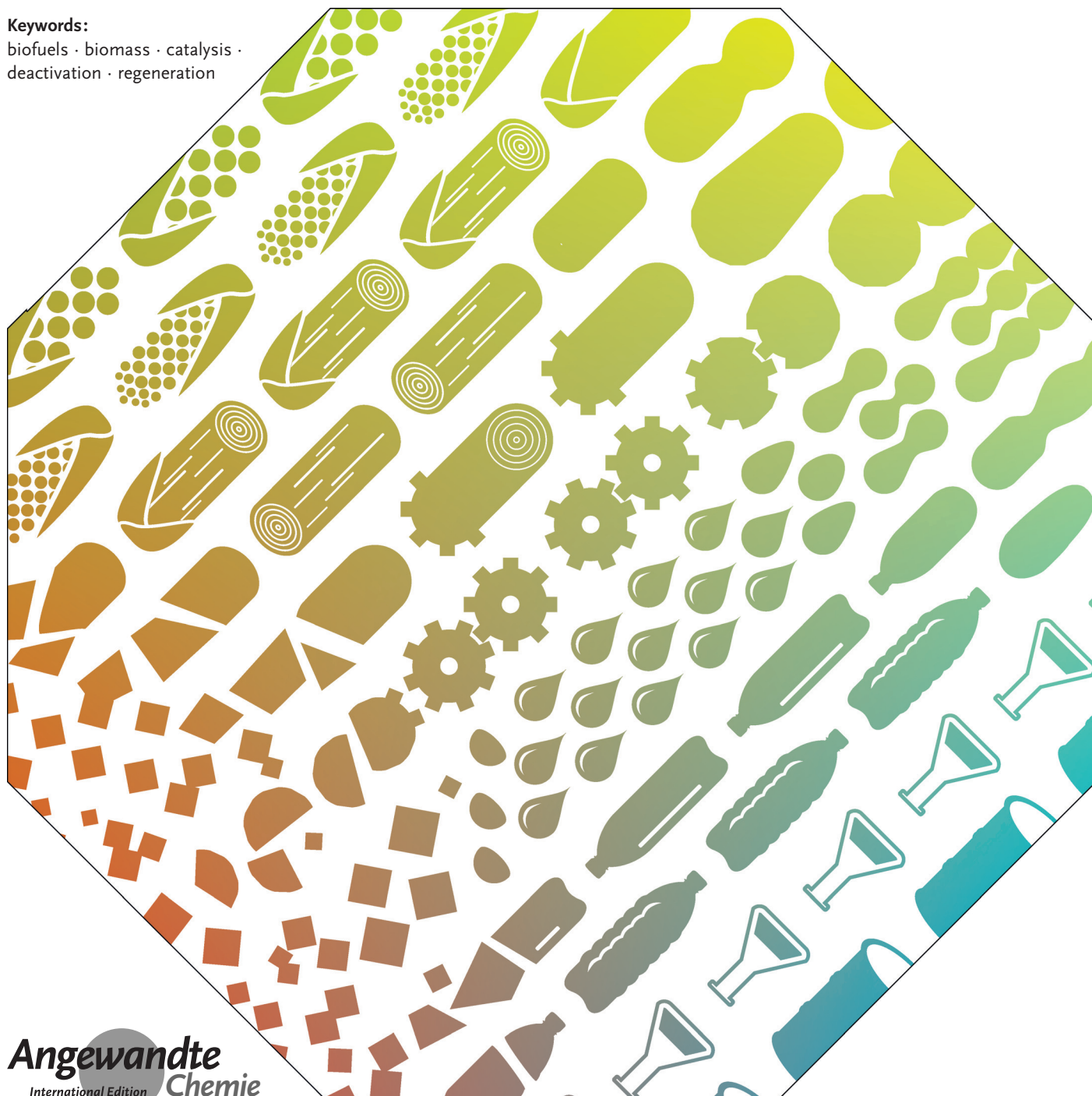


Renewable Feedstocks: The Problem of Catalyst Deactivation and its Mitigation

Jean-Paul Lange*

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Much research has been carried out in the last decade to convert bio-based feedstock into fuels and chemicals. Most of the research focuses on developing active and selective catalysts, with much less attention devoted to their long-term stability. This Review considers the main challenges in long-term catalyst stability, discusses some fundamentals, and presents options for their mitigation. Three main challenges are discussed: catalyst fouling, catalyst poisoning, and catalyst destruction. Fouling is generally related to the deposition of insoluble components present in the feed or formed by degradation of the feed or intermediates. Poisoning is related to the deposition of electropositive contaminants (e.g. alkali and alkaline earth metals) on acid sites or of electronegative contaminants (e.g. N and S) at hydrogenation sites. Catalyst destruction results from the thermodynamic instability of most oxidic supports, solid acids/bases, and hydrogenation functions under hydrothermal conditions.

1. Introduction

1.1. Renaissance of Biomass Valorization

The past decade has witnessed an impressive increase in research aimed at converting biomass into fuels and chemicals. Numerous authoritative reviews have discussed the conversion of lignocellulose, carbohydrates, lignin, and triglycerides.^[1–12] The literature often focuses on the chemistry of the conversion and the catalyst design required to achieve it. However, it only sporadically discusses challenges encountered in the long-term operation of the catalysts. Biomass feedstock, nevertheless, brings quite a large number of challenges for long-term and steady-state operation with conventional catalysts. As in the case of fossil feedstock, biomass streams can still be complex, polymeric, and significantly contaminated. However, they are also overfunctionalized and thermally unstable. Furthermore, they may require polar/aqueous and corrosive operating conditions. All these characteristics are challenging for the long-term operation of catalysts and processes.

The present Review will discuss some of these stability challenges, will consider the sporadic information reported in the literature on this matter, and will complement the discussion by observations gathered at Shell during some 15 years of research on lignocellulosic biofuels. The discussion will be organized around three major sources of deactivation:

- fouling by heavy components that are either present in the feed or formed upon thermal degradation of the feed,
- catalyst poisoning by contaminants that are either present in the feed or come from the processing unit, and
- catalyst degradation, for example, by sintering, leaching, or support degradation, which results from operation in a corrosive polar medium.

Beyond addressing the challenges, the Review will also discuss potential solutions whenever possible. Catalyst deactivation is clearly not a specific feature of bio-based processes. It has been widely encountered in oil and petrochemical

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processes and extensively discussed in numerous reviews and books.^[13,14]

1.2. Economic and Industrial Guidelines

Before focusing on the challenges in catalyst stability, it seems valuable to look back to the decades of industrial practice in fuel and chemical manufacturing to identify performance or operational windows that are suitable for industrial practice and that will, most likely, also apply to biomass conversion processes. This can be done by revisiting some economic and industrial guidelines that were formulated more than ten years ago after analysis of a large set of industrial processes.^[15] The guidelines will be extended beyond the direct scope of this Review, that is, catalyst deactivation, to cover catalyst selectivity, activity, and feed dilution (Table 1), as these additional criteria will occasionally offer a valuable industrial context for assessing some of the mitigation options presented.

In terms of catalyst stability—the topic of this Review—fuel and chemical manufacturing processes appear to operate over a large window of catalyst life, namely from several years down to less than one hour. Multiyear operation is common for fixed-bed processes, while short catalyst life is encountered in fluid catalytic cracking (FCC) and olefin polymerization. This catalyst life occasionally includes multiple catalyst regeneration cycles, which can proceed after several months of operation or after only a few seconds. In fact, the important performance criterium is not the overall catalyst life or its life in a single cycle. It is really its overall productivity: the industrial processes all seem to operate such that the catalyst produces 10^3 – 10^4 times its own weight of products before being disposed of. So a very active catalyst can be disposed of very rapidly, as is done for polymerization catalysts, which are often left inside the polymer they produce. In contrast, a “slow” catalyst would be run for a few years before disposal.

In terms of the catalyst activity, industrial practice accommodates a large window of activity that stretches

[*] Prof. Dr. J.-P. Lange
Shell Research and Technology Center
Grasweg 10, HW 1031, Amsterdam (The Netherlands)
E-mail: jean-paul.lange@shell.com

Table 1: Performance windows applied in fuel and chemical manufacturing processes (not including biotechnology).^[15]

	Industrial window	Comments
stability	1–10 t _{prod.} kg _{cat.} ⁻¹	catalysts with low activity (0.2 t/t/h) require a long life time (> 1 y); catalysts with high activity (> 100 t/t/h) can have a short life time (< 1 h)
activity	0.1–10 t _{prod.} / (m ³ _{react} h)	catalysts with low activity (0.2 t/t/h) require high concentrations (ca. 1 t _{cat.} m ⁻³); catalysts with high activity (> 100 t/t/h) need a low concentration (< 1 kg m ⁻³)
selectivity	70–100 wt%	Sel. > (feed price + NX)/product price; N = number of process steps; X = upgrading cost per step (e.g. ca. \$200 t ⁻¹)
feed concentration	3–100 wt%	undiluted feed is preferred; feed dilution for highly endo/exothermic ($ \Delta H_{\text{react}} > 10 \text{ kJ g}_{\text{prod}}^{-1}$) and fast reactions

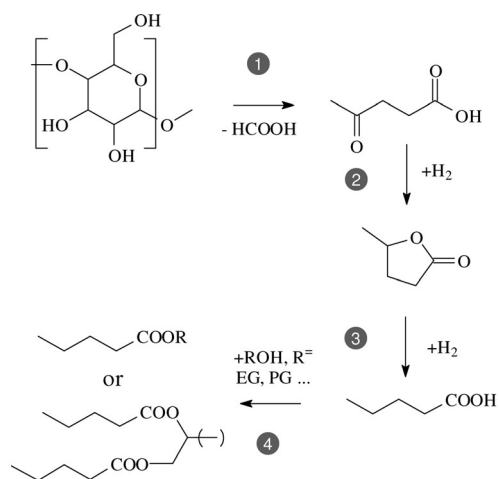
from a space-time-yield of about 0.2 ton product per ton catalyst per hour up to > 100 t/t/h. More critical, however, is the overall reactor productivity, for this is typically contained within a narrower window of 0.1 to 10 ton of product per m³ reactor per hour. The lower limit is set by an excessive reactor size and cost, whereas the upper limit is often set by mass or heat transfer. Accordingly, the catalyst activity is balanced by its loading into the reactor to meet the reactor productivity window: very active catalysts are operated in high dilution (< 1 kg m⁻³ or < 0.1 wt%), while poorly active catalysts are operated at high loading, for example, in fixed-bed reactors of approximately 1 t m⁻³.

The catalyst selectivity is often the most critical feature, particularly when using expensive feedstock: the lower the selectivity, the higher the feedstock consumption and cost. In fact, a selectivity target can be easily estimated on the basis of the feed and product price and a modest cost penalty for carrying out the conversion (see Table 1). However, this would neglect the impact that poor selectivity can have on heat management and product separation/purification, which can be very significant.^[15] Consequently, selectivities below 70 % (by weight of feed) are rarely encountered in industry.

Finally, we should not forget the importance of feed dilution. Dilution of the feed is indeed avoided as much as possible, as it increases the size (and cost) of the equipment and may complicate the recovery and purification of the products. Feed dilution may, nevertheless, be convenient for highly exothermic or endothermic reactions that proceed at very high rates, since the dilution may assist the removal or

supply of heat to the catalyst. For example, feed concentrations of a few wt% are encountered for exothermic reactions that release more than 10 kJ g⁻¹ product.^[15]

There is no clear reason why these various performance criteria would not apply to biomass conversion processes. For example, they appear to be handy for analyzing the complex manufacturing of valeric acid based biofuels from lignocellulose, as illustrated in Figure 1.^[16] They indeed helped to identify the very first step, the conversion of lignocellulose into levulinic acid (“1. hydrolysis” in Figure 1), as the technical bottleneck of the whole chain because of its low selectivity, low productivity, and low product concentration.



	1. Hydrolysis	2. Hydrogen.	3. Hydrogen.	4. Esterific.
Catalyst	H ₂ SO ₄	Pt/TiO ₂	Pt/ZSM-5	IER
Selectivity	mol%	50–60%	>95%	>95%
Productivity	t m ⁻³ h ⁻¹	>0.1/h	>10/h	>1/h
Concentration	wt %	<5%	>90%	>50%

Figure 1. Reaction scheme and key performance factors for converting lignocellulose into valeric acid based biofuels (adapted from Ref. [16]; [a] the low productivity of step 4 is due to the reactive distillation which integrates reaction and separation).



Jean-Paul Lange studied at the university of Namur (Belgium), obtained his PhD in chemistry at the Fritz-Haber Institute (Berlin, Germany), and was a postdoctoral fellow at the Lehigh University (Pennsylvania/US). He is currently principal research scientist at Shell, where he has been exploring novel catalytic processes for the conversion of natural gas, manufacture of chemicals, and the conversion of biomass into fuels and chemicals for more than 25 years. He is also Professor in Chemical Biorefining at the University of Twente.

2. Catalyst Fouling

One of the challenges often encountered in processing bio-based feedstock arises from fouling of the equipment and catalyst. This fouling is caused by the deposition of heavy insoluble materials that are either present in the feedstock or are formed in situ by decomposition of the feedstock.

Such fouling has been reported for the upgrading of bio-oil, as reviewed by Elliott et al.^[17] in 1991 and “rediscovered” more recently when co-processing various types of pyrolysis oils with vacuum gasoil (VGO) in a laboratory-sized FCC unit.^[18] Catalyst fouling is also observed when processing sugars,^[19,41] sugar derivatives,^[20–22] vegetable oils,^[23] and crude glycerol.^[68]

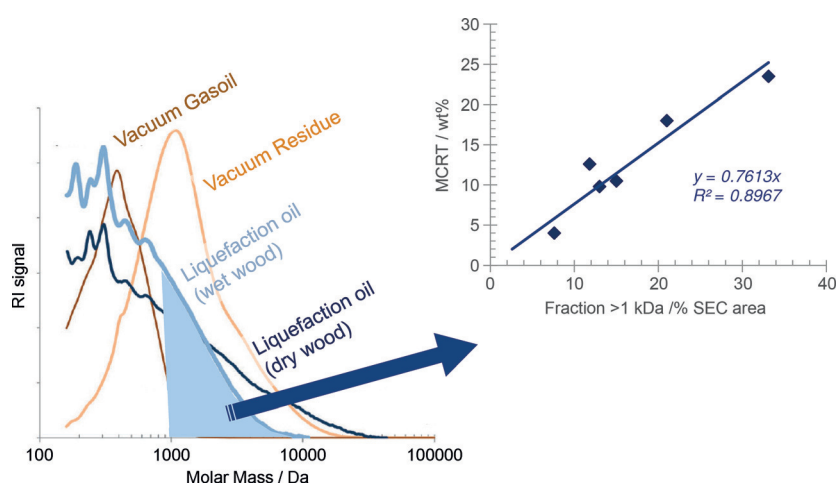


Figure 2. Heavy components determine the coking tendency of biomass streams (adapted from Ref. [26]). The insert illustrates the relationship between the fraction of heavy products, expressed as fraction of the size exclusion chromatograph (SEC), and the coking tendency of the stream, expressed as Micro Carbon Residue fraction (MCRT).

2.1. Fouling by Heavy Components

Fouling is not a new challenge that is limited to the processing of biomass streams. Refinery technologists have encountered it abundantly in refinery processes. Fouling by heavy oil components, called asphaltenes, is encountered when transporting, handling, and/or upgrading heavy oil.^[24,25] Fouling is typically due to precipitation of asphaltenes because of a change in the conditions (e.g. temperature), composition, or acidity of the stream. In residue hydroprocessing, for example, the residue undergoes significant hydrogenation and, thereby, loses its capacity to keep the heavy aromatic asphaltenes properly dissolved. This often results in deposition of asphaltenes and severe catalyst and reactor fouling.^[25] Similar dissolution issues may also be expected for biomass hydroprocessing.

Refiners have developed simple pyrolysis tests, for example, the Micro Carbon Residue (MCR) test, to evaluate the coking tendency of their process feed. These tests are equally applicable to biomass streams. For example, the coke yield reported for FCC processing of blends of VGO and pyrolysis oil show a good correlation with the MCR results.^[18] Studies in our laboratories revealed that the coking tendency of bio-oil also correlates with the fraction of the heaviest components of various bio-oils. For example, Figure 2 shows that the MCR correlates with the fraction of component that has an apparent molecular weight above 1 kDa, as measured by size-exclusion chromatography (using polystyrene and M_w standards). This finding suggests that the coke precursors are components that are too heavy and too refractory to crack and evaporate at high temperature.

2.2. Fouling by Degradation

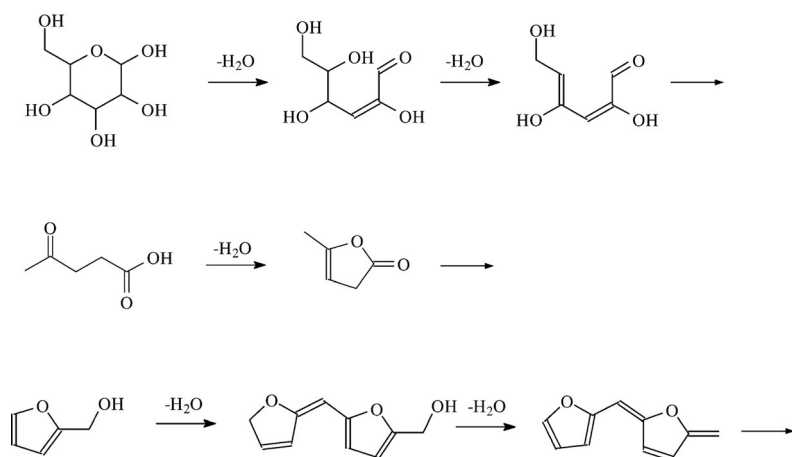
Another mechanism for fouling is the decomposition of unstable feed components or reaction intermediates, which leads to in situ formation of heavy products and, eventually, their deposition on hot surfaces or on the catalyst. Biomass

streams are particularly prone to such fouling mechanisms because they are often highly functionalized and, thereby, very reactive. A few examples are discussed below and summarized in Figure 3.

Sugars are known to undergo thermal decomposition, also called caramelization, at elevated temperature. This even occurs in hot water. Ketoses degrade above about 110 °C while aldoses degrade above 160 °C.^[27] Caramelization involves a complex set of reactions that includes dehydration, condensation, and rearrangement reactions that lead to heavy, unsaturated, and colored products that deposit on the reaction vessel and on the catalyst.^[28]

Many sugar derivatives appear to be sensitive to thermal degradation. For example, levulinic acid is converted into the unsaturated angelica lactone at elevated temperatures. During our research program on the upgrading of levulinic acid, we observed rapid deactivation of the catalyst above 200 °C. Control experiments, that is, with the reactor filled with inert material, also resulted in the formation of colored components with high molecular weights (measured by size-exclusion chromatography) in the reactor effluent. These are likely formed by condensation reactions of the angelica lactone.

Similarly, the processing of furfural at high temperatures (>250 °C) under a hydrogen atmosphere is often accompanied by the formation of colored compounds, which eventually lead to reactor fouling and plugging. Here, simple thermal runs with furfural showed no significant decomposition under these conditions but similar runs with furfuryl alcohols did. Hence, the reactor fouling is likely due to intermediary formation of furfuryl alcohol. Furfuryl alcohol is indeed known to condense into furanic resin under acidic conditions at mild temperature.^[29] Similar reactions are likely to proceed thermally at elevated temperatures. Our upgrading process produced furfuryl alcohol as a reaction intermediate and, presumably, led to its subsequent oligomerization under the reaction conditions.



Degradation

Ketose
>110°C

Aldose
>160°C

Levulinic acid
>200°C

Furfuryl alcohol
>250°C

cosolvents such as γ -valerolactone (GVL), acetic acid, or methyl tetrahydrofuran (mTHF) can depress the formation of humins even at high lignocellulose concentrations (Figure 4).^[33] The beneficial effect of GVL as a cosolvent for reducing the amount of insoluble humins was later confirmed by the group of Dumesic.^[34]

Fouling by heavy feed components may also be depressed by selective removal of the heavy contaminants or the avoidance of excessive temperatures. For example, heavy bio-oil components can be removed by means of tem-

Figure 3. The decomposition of biomass intermediates to reactive unsaturated components leads to fouling.

2.3. Measures To Mitigate Fouling

The measures taken against fouling will of course depend on the intrinsic source of fouling. Elliott et al. reported successful runs in the hydrotreatment of bio-oil by performing the hydrotreatment in two steps, a first step at low temperature followed by a second step at high temperature.^[17] The initial low-temperature step is expected to allow the hydrogenation of reactive unsaturated components such as carbonyl groups, dienes, or furans that would otherwise undergo oligomerization reactions at higher temperature. Such a two-step strategy has been confirmed to be successful for the hydrotreatment of pyrolysis oil^[18] as well as the hydrodeoxygenation of furanic oligomers.^[30,31] Similarly, the hydrogenolysis of sugars to small glycols and other short oxygenates proceeds more effectively by hydrogenating the sugar to sugar alcohols at mild temperatures and, subsequently, cracking the sugar alcohol to shorter oxygenates at higher temperatures.^[32]

An alternative mitigation option is, of course, dilution of the feed. Operation with a highly diluted solution is likely to hinder fouling by depressing the oligomerization reaction of the feed or its degradation product. For example, the acid hydrolysis of lignocellulose to levulinic acid is known to be accompanied by the undesired production of degradation products (humins) that lead to severe fouling of the reactor. The generation of humins as by-products and the resulting fouling can be significantly depressed by lowering the concentration of lignocellulose (Figure 4). However, dilution of the feed may present severe economic penalties in terms of equipment size and separation cost, as discussed in Section 1.2.

Another approach to mitigate fouling is to ensure effective dissolution of the heavy components. This can be attempted by selecting a suitable cosolvent. In the case of the acid hydrolysis of lignocellulose, the addition of organic

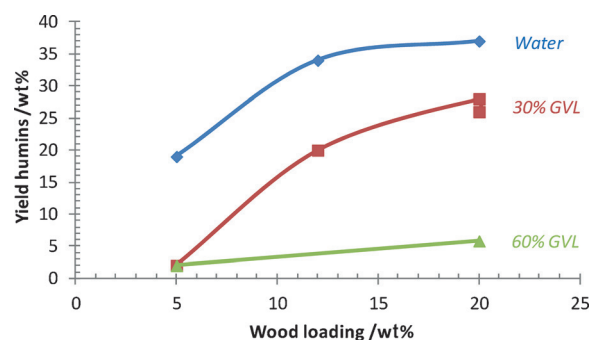


Figure 4. Effect of dilution and cosolvent on condensation reactions during the acid hydrolysis of lignocellulose to levulinic acid (5–20 wt% birch wood in water and water/ γ -valerolactone (GVL) with 3 wt% H_2SO_4 at 200°C).^[33]

perature-swing extraction.^[35] This allowed the successful recycling of the bio-oil as a liquefaction medium with a marginal build-up of heavy product and a marginal increase in the viscosity of the liquefaction medium.^[36] Alternatively, crude glycerol can be purified from heavy organic (and inorganic) contaminants by treatment with acrolein to form a ketal, which can be evaporated at mild temperatures.^[70]

Although fouling can be reduced, it can rarely be avoided; hence, catalyst regeneration will likely be required. Fouled catalysts are generally (partly) regenerated by means of coke burn off, as commonly practiced in oil refining. However, solvent wash has occasionally been successful in regenerating catalysts that were operated at mild temperatures. Moreover, hot hydrogen treatment has been found to be equally successful, and simpler, than coke burn off in regenerating coked catalysts.^[14,19,37]

3. Catalyst Poisoning

3.1. Source of Contaminants

Lignocellulosic biomass is generally described in terms of cellulose, hemicellulose, and lignin content. Minor, although critical, contaminants are often forgotten, however. For example, N can account to up to 1 wt %, while S can account for some 0.2 wt % of the biomass, particularly in the case of grasses and agricultural residue (Table 2). These electro-

Table 2: Contaminants present in bio-feedstock.

Composition		Hard wood	Soft wood	Grasses	Starch
cellulose	wt%	ca. 35	ca. 40	ca. 35	ca. 5
hemicellulose	wt%	ca. 22	ca. 20	ca. 23	> 85 (starch)
lignin	wt%	ca. 25	ca. 28	ca. 22	< 0.5
N	wt%	0.1–0.5	0.1–0.2	0.5–1.5	0.02–0.5
S	wt%	< 0.1	< 0.2	< 0.2	< 0.1
ash	wt%	< 1	< 2	< 10	< 0.5
Basicity ^[a]	wt%	< 1	< 0.5	1–5	< 2
Ca	ppm	700–1000	200	1000–3000	50–300
K	ppm	300–500	100	2000–10000	50–1000
Mg	ppm	100–300	50	50–100	20–200
Na	ppm	20	10	20–100	50–500

[a] Basicity: g H₂SO₄ needed to neutralize 100 g biomass.

negative elements together with Cl, which is also present in biomass, are infamous for their potential to poison metal catalysts used for hydrogenations. The biomass also contains electropositive contaminants such as Ca²⁺ and K⁺ in levels that can exceed 0.1 wt % (1000 ppm). These contaminants (together with basic N) can neutralize the strong homogeneous or heterogeneous acids needed for biomass conversion, for example, for hydrolysis or catalytic pyrolysis. In fact, through its basic cations, 100 g of lignocellulose has the potential to titrate about 0.5 g of H₂SO₄ in the case of wood and up to 5 g in the case of grasses (Table 2). Even starches are contaminated with various electropositive and -negative elements such as K, N, and S. These contaminants are, therefore, likely to intervene in the primary biomass conversion process. However, they may also find their way into the product streams and, thereby, also play a role in downstream upgrading processes.

Besides the biogenic contaminants, bio-based processes may also suffer from external contaminants, for example, impurities that originate from previous processing steps or from vessels and piping that are attacked by the acidic and corrosive biomass stream.

Examples of both types of poisoning have been reported. About two decades ago, Arena reported on the deactivation of a Ru-based catalyst by S, Fe, and gluconic acid during the hydrogenation of glucose to sorbitol.^[38] The S came from the feed (15 ppm), the Fe came from the wall of the steel reactor (as confirmed by mitigation when using a teflon-coated reactor), and gluconic acid was formed in situ (as confirmed by mitigation with deep feed deoxygenation). A decade later, Elliott et al.^[39] extended the study of catalyst contamination to the hydrogenation of glucose to give sorbitol. They

reported severe catalyst poisoning by amino acids as well as NH₄⁺ and Ca²⁺ cations, and moderate poisoning by NO₃⁻ anions. In contrast, K⁺, SO₄²⁻, PO₄³⁻, and Cl⁻ ions did not seem to affect the catalysis. Claus and co-workers^[40] confirmed the interference of external poisons in the slow deactivation of a Ru/Al₂O₃ catalyst by Fe, Si, and Zr, which was attributed to the SS316 material used for the reaction setup. More recently, Metkar et al.^[41] reported the deactivation of acidic zeolite catalysts by alkali and alkaline earth (K, Mg, Ca) contaminants present in real hydrolysate when

exploring the conversion of xylose into furfural under catalytic distillation conditions. The deactivation could be mitigated by a) a combination of feed cleaning with ion-exchange resins, b) catalyst regeneration by coke burn off, and c) an acid wash for reacidification. As a last example, crude glycerol is obtained by the alcoholysis of triglycerides, and is generally contaminated by various components, including catalyst residue (in this case, Na salts).^[68] These contaminants can deactivate the catalysts needed for upgrading glycerol, for example, to acrolein. Dubois and

co-workers^[69] proposed removing these salt by distilling the crude glycerol in a fluidized bed of inert particles to trap-fix the salt and heavy organic contaminants. The fluidized particles could then be regenerated by acid wash and coke burn off.

We have also encountered both types of poisoning in our own research, and will illustrate it for the hydrogenation of levulinic acid to γ -valerolactone and its subsequent conversion. Analytical grade levulinic acid appeared to contain various degrees of contaminants, depending on the supplier. Besides containing Al, Ca, and P, which are found in all sources, some sources also contained S (ca. 8 ppm) and “steel contaminants” (1.4 ppm Fe, 0.2 ppm Cr, 0.2 ppm Ni). The hydrogenation of levulinic acid to γ -valerolactone was carried out under gas-phase conditions using a PtRe/ZrO₂ catalyst.^[16] The catalyst appeared to suffer from slow deactivation over time and could not be fully regenerated by simple coke burn-off. Analysis of the spent catalyst by X-ray photoelectron spectroscopy (XPS) revealed accumulation of S (2.5 atom per 100 atom Zr) and “steel components” (1.5 atom Ni and Fe per 100 atom Zr) as well as traces of foreign metals such as Cu, Zn, Pb, and Sn.

3.2. Mitigation

The mitigation of such poisoning may require thorough washing of the feed, the use of appropriate cation/anion exchangers, or a guard bed. An example of the use of washing is the extraction of heavy metals by supercritical CO₂ in the presence or organic complexing agents. This approach was developed for cleaning liquid/aqueous system,^[65] but has also

been applied to clean solid materials such as coal^[66] and wood.^[67] Much research is needed to achieve satisfactory cleaning at low cost, particularly when dealing with solid biomass.

The selection of proper equipment metallurgy is imperative for minimizing external poisons and, more importantly, for safe operation. As demonstrated by Arena,^[38] proper deoxygenation of the feedstock can prevent the formation of carboxylic acids which could poison the catalyst directly or indirectly by attacking the metallurgy.

4. Catalyst Destruction

Besides fouling by heavy/unstable feed and poisoning by electronegative/positive contaminants, biomass processing technologists also need to consider the reaction medium in which the conversion will be carried out. More than often, the conversion process will be carried out in water or polar and protic media to allow proper dissolution of the polar feed, reaction intermediates, and/or product. Moreover, the medium will often be acidic, for example, to favor the deoxygenation of the feedstock by means of dehydration or because the carbohydrates are (partly) converted into carboxylic acids. Such an environment deviates severely from the hydrocarbon medium used in the petrochemical industry and in oil refineries, for which most of the catalysts have so far been developed and optimized. So, it should be no surprise that the conventional catalysts and processes encounter challenges in biomass processing.

These challenges were recognized by biomass pioneers some 20 years ago already. For example, Elliott et al.^[42] studied the gasification of biomass in near-critical water and observed the degradation of numerous catalysts. Co- and Fe-based catalysts were found to undergo reoxidation, while Ni- and Ru-based catalysts remained in a reduced state under such conditions. Similarly, SiO₂ and γ-Al₂O₃ supports decomposed, while α-Al₂O₃, ZrO₂, and C survived the conditions.

More examples are still being published today. For example, Ni/SiO₂ degraded during the hydrogenation of glucose to sorbitol, while Ru/Al₂O₃ seemed stable.^[40] Indeed, the Ni/SiO₂ catalyst suffered from extensive leaching of Ni and sintering of the SiO₂. Similarly, carbon-supported Ni₂P and Ni/W₂C catalysts applied for the hydrogenolysis of cellulose to sorbitol or ethanediol were reported to degrade by decomposition of the carbide phase and leaching of Ni, W, and P.^[43,44] Acidic supports such as amorphous silica-alumina (ASA) and zeolites are more stable than silica and alumina in hot liquid water. However, they still undergo severe degradation through hydrolysis of the Si-O-Si bonds.^[45] ASAs prepared by co-gelation lose their microporous structure, whereas ASAs prepared by deposition-precipitation resist better as a consequence of the conversion of their Al-rich shell into protective böhmite clusters. Y zeolite (Si/Al > 14) is converted into amorphous material in hot water at 150–200 °C, whereas other zeolites, for example, ZMS-5 (Si/Al = 25) and LaY (Si/AL = 5), are stable for several hours.^[46] Very recently, Datye and co-workers provided a comprehensive review on the hydrothermal stability of heterogeneous

catalysts for biomass conversion.^[47] All these observations justify a reconsideration of the thermodynamics of catalyst stability, both of the catalyst support and the hydrogenation function. Although we will focus on the aqueous thermodynamics of the support and hydrogenation function below, one should not forget the potential role that dissolved organic components can play as chelating or clathrating ligands to stabilize metal cations in solution and, thereby, enhance the leaching and destruction of the catalyst. Multifunctional acids such as diacids, hydroxyacids, or amino acids as well as other multifunctional organic compounds (e.g. polyols or acetyl acetate) should be highly suspect in this regards.^[71,72]

4.1. Oxidic Supports

The literature indicates that carbon-based supports are the most promising materials for hydrothermal conditions. However, they still show significant disadvantages over conventional oxidic materials, for example, the impossibility to regenerate a catalyst by coke burn-off or limited mechanical strength. Hence, catalyst technologists are still searching for oxidic supports that can resist hydrothermal conditions.

The search for oxide materials can start by considering their water solubility at ambient temperature. According to the literature,^[48] simple metal oxides and hydroxides show a water solubility that varies over about 16 orders of magnitude. Ranking the solubility data according to the electronegativity of the corresponding oxide (or hydroxide) reveals a clear trend: oxides with either a very low or very high electronegativity are highly soluble, while those with an electronegativity close to that of water are reasonably to completely insoluble in cold water (Figure 5; the electro-

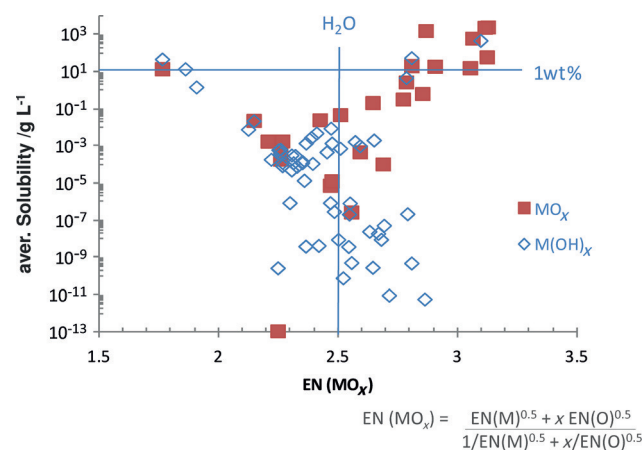


Figure 5. Solubility of oxides and hydroxides in cold water (data from Ref. [48]).

negativity of the corresponding oxide EN(MO_x) is calculated as discussed in the appendix). This trend is quite sensible, as the very basic and acidic oxides are likely to dissociate in water to form hydroxides that are more soluble than the oxide, particularly when protonated or deprotonated to cationic or anionic species, depending on the effective

pH value. Consequently, highly acidic or basic supports are not likely to survive hydrothermal conditions.

This analysis is not limited to the support, but can also be extended to possible catalyst promoters. A corollary of this discussion is that the use of a solid acid or base for the catalytic conversion of biomass under hydrothermal conditions will likely present severe challenges in terms of catalyst stability.

After discarding oxides with a too low and too high EN(MO_x) value, the selection of the support can be refined using the electrochemical Pourbaix diagrams. These diagrams map the thermodynamically most stable phases for a given window of pH values and electrochemical potentials. The electrochemical potential represents the redox potential of the environment and highlights two reference cases, the oxidation of H₂O to O₂/H⁺ and its reduction to H₂/OH⁻, which are given by two dotted diagonal lines on the Pourbaix diagrams.

When calculated for 200 °C, the Pourbaix diagrams of SiO₂, Al₂O₃, TiO₂, and ZrO₂ provide the following conclusions (Figure 6). SiO₂ appears to be unstable, as it is converted

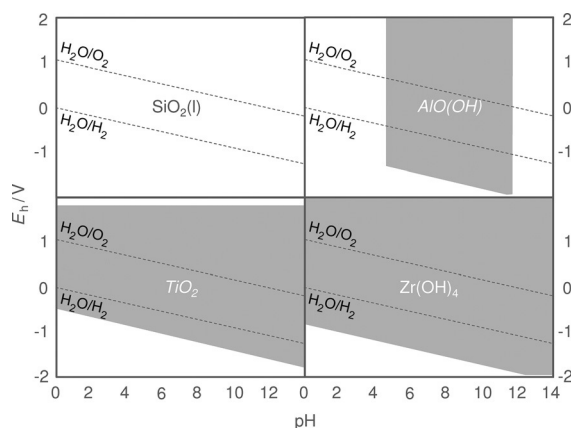


Figure 6. Window of stability of typical metal oxide supports in hot water at 200 °C (calculated by HSC Chemistry 7.1).

into silica gel at all pH values in pressurized water at 200 °C. Al₂O₃ and ZrO₂ are converted into their hydrate forms, that is, to Böhmite AlO(OH) (at a pH value between 4.5 and 11.5) or to Zr(OH)₄ (over the whole pH range). In contrast, TiO₂ seems to be stable over nearly the entire pH window. The analysis of numerous oxides using Pourbaix diagrams furthermore confirmed the conclusions drawn above from Figure 5: strongly acidic and basic oxides are unstable under hydrothermal conditions.

It should be stressed that the data available most likely describe the thermodynamically most stable phase and, therefore, might not be totally applicable to metastable phases, which are often obtained when preparing high surface-area materials. Consequently, the diagrams reported in Figure 6 don't provide insight into possible recrystallization and/or sintering of the metal oxide under hydrothermal conditions. Such consideration will require us to push the analysis to a third and finer level.

4.2. Hydrogenation Function

The Pourbaix diagrams are also a powerful approach to investigate the stability of the hydrogenation function of catalysts. According to Figure 7, Ni and Co are in a metallic

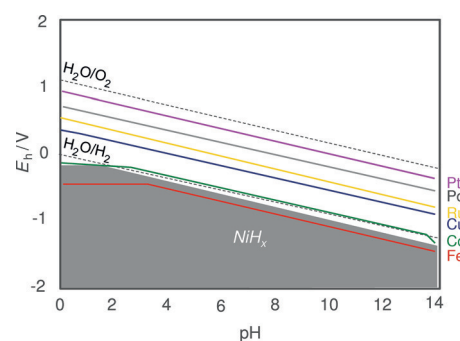


Figure 7. Stability window of hydrogenation metals in hot water at 200 °C (calculated by HSC Chemistry 5.11).

state over a wide pH range at the H₂O/H₂ electropotential at 200 °C, which is representative for atmospheric H₂ pressure. This contrasts with Fe, which requires a more negative reduction potential to be reduced to its metallic state. However, Cu and the heavier Group 8–11 metals are all in their metallic state under reducing conditions. These results suggest risks of reoxidation, leaching, and/or sintering for the least-noble hydrogenation metals Fe, Co, Ni, and possibly also Cu. Such behavior was indeed reported in the literature for supported Ni catalysts operating under hydrothermal conditions, as mentioned previously.^[40,42]

Such a thermodynamic evaluation can be extended to nonmetallic phases that are known to be active for hydrogenation reactions in hydrocarbon environments. For example, metal sulfides are applied on a large scale for hydrodesulfurization in oil refineries.^[49,50] Tungsten and molybdenum carbides and nitrides have been reported to exhibit Pt-like activities for various hydrogenation, hydrogenolysis, and hydroisomerization reactions.^[51–53] Furthermore, various metal phosphides have been shown to catalyze the hydrodeoxygenation of bio-based intermediates.^[54] Regrettably, all these nonmetallic phases appear to be metastable or truly unstable under hydrothermal conditions.

The inclusion of S or P, for example, into the thermodynamic calculations results in the appearance of Mo sulfides and Ni phosphide phases where metallic species were expected and not where oxidic species were dominating (Figure 8). Hence, these composites should be equally prone to oxidation as the pure metallic species under hydrothermal conditions. The inclusion of C or N is even more striking: no stable composites are observed under hydrothermal conditions. Carbides and nitrides of Group 6–10 metals are less stable than the corresponding metal or metal oxides under hydrothermal conditions. Consistently with these findings, Zhang and co-workers reported the leaching of W and Ni from supported Ni/W₂C during the conversion of cellulose into ethenediol.^[43,44]

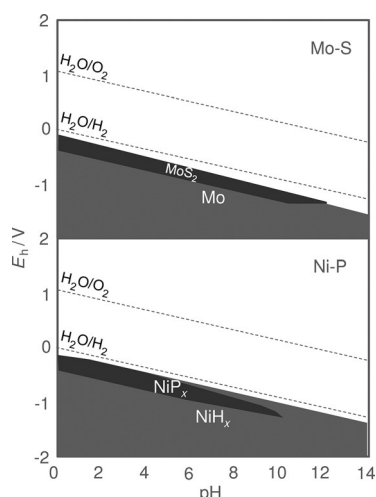


Figure 8. Window of stability of metal sulfides or phosphides (calculated by HSC Chemistry 5.11).

In summary, the hydrothermal conditions seem to limit the choice of hydrogenation functions to noble metals and possibly also Cu. Non-noble metals and their composites (i.e. carbides, nitrides, phosphides, and sulfides) are expected to undergo reoxidation to the oxides/hydroxides and, eventually, leach or sinter. Similar risks are expected for processes with superheated steam, although likely to a lesser extent.

4.3. Beyond Bulk Thermodynamics

Although very insightful, the Pourbaix diagrams and other thermodynamic calculations should be used with caution. Indeed, additional effects may significantly influence the stability of catalysts.

For example, the Pourbaix diagrams use thermodynamic data that are measured from bulk, millimeter-sized materials. They may not fully apply to nanoparticles used in catalysis. A limited number of studies indeed suggest different stability windows for nanoparticles. For example, Navrotsky and co-workers^[55] investigated the effect of particle size on TiO₂ phases and showed the rutile phase to be the most stable phase for large particles, while the anatase phase is the most stable for small particles with a high surface area (Figure 9, left). Such a change in stability has been attributed to the increasing role that surface tension takes in the overall

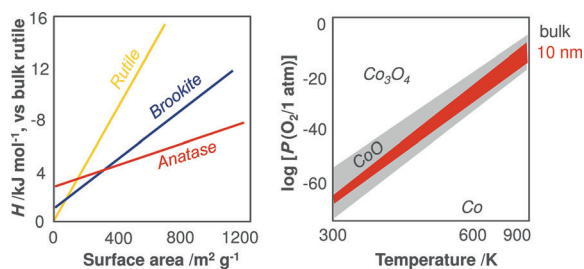


Figure 9. Thermodynamic stability of nanoparticles (adapted from Refs. [56, 57]).

thermodynamics of the particles. Navrotsky et al.^[56] also compared the stability of bulk and nanostructured Co phases and found that nanoparticles are more difficult to reduce from Co₃O₄ to CoO but easier to reduce further to metallic Co, as illustrated in Figure 9, right.

Besides thermodynamics, one can also consider and influence the kinetics of dissolution. The approaches of “kinetic stabilization” reported so far consist of coating or encapsulating the catalyst. For example, Resasco and co-workers^[57] protected a H-Y zeolite by rendering it hydrophobic and, thereby, improved its stability for the alkylation of *o*-cresol with propanol in a biphasic medium (water/decalin) (Figure 10, top). The “hydrophobization” of the zeolite was achieved by silylating its external surface with organosilane components such as octadecyltrichlorosilane (OTS).

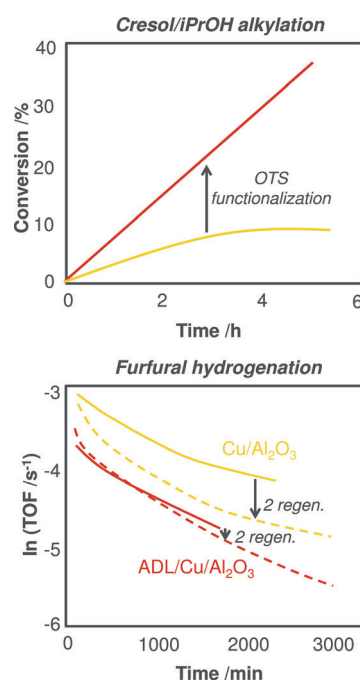


Figure 10. “Kinetic stabilization” of catalysts by functionalization of HY zeolite with OTS (top) or atomic layer deposition (ADL) of Cu/Al₂O₃ (bottom; TOF = turnover frequency; adapted from Refs. [58, 64]).

Hydrophobic coatings have also been achieved by pyrolysis of sugar-coated oxides. For example, such carbon coating was claimed to depress the hydration of γ -Al₂O₃ to Böhmite and maintain its surface area after a 12 h treatment in hot water at 200 °C.^[58] Similarly, Lin et al.^[59] prepared Ni/TiO₂ coated with hydrophobic carbon layers to prevent the formation of nickel hydroxide. Consequently, the nickel sites remained very active and the catalyst could be recycled in the hydrogenation of nitrobenzene in the presence of water solvent. Interestingly, a similar protection could also be achieved in situ during the conversion of biomass streams. For example, the presence of glycerol, sorbitol, phenolic components, and lignin is reported to retard the hydration of γ -Al₂O₃ to Böhmite by forming a carbonaceous deposit.^[60,61]

As an alternative to hydrophobization, surface doping with inorganic components is also claimed to stabilize catalysts against sintering or degradation. For example, the presence of Ni or Pt deposited on the γ - Al_2O_3 slows down its hydration to Boehmite.^[62] Dumesic and co-workers^[63] protected a $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst against Cu leaching by coating it with a porous atomic layer of Al_2O_3 through atomic layer deposition (ALD; Figure 10, bottom). When applied to the hydrogenation of furfural in *n*-butanol at 140 °C, the catalyst was still deactivated by coking, but was successfully regenerated by coke-burn off without a clear sign of Cu sintering or leaching.

Although very promising at this stage, the approach of “kinetic stabilization” still needs to prove its effectiveness for a lifetime productivity of 1 ton of product per kg of catalyst, as discussed in Section 1.2.

5. Summary and Outlook

The discussion presented in this Review illustrates some of the challenges that catalyst scientists and technologists are facing in converting bio-based streams into fuels and chemicals.

The process can suffer from fouling as a result of the deposition of heavy and poorly soluble materials onto equipment components and catalysts. The heavy components may be present in the feed, as encountered, for example, when processing bio-oils. However, they may also form by the decomposition and condensation of reactive feed components and/or intermediates. Potential mitigations can be sought by applying low concentration, low operation temperatures, the use of mild hydrogenation conditions to stabilize reactive species, or the use of a cosolvent to secure the proper solubilization of heavy components.

Bio-based processes can also suffer from poisoning by feed impurities (e.g. basic cations or N, which neutralize acidic catalytic sites) or electronegative elements (e.g. N or S that poison hydrogenation sites). Proper treatment of the feed is necessary, but often quite expensive. Catalysts can also be poisoned by cationic species that originate from vessels and piping when attacked by the corrosive medium, by acidic intermediates, or by-product. Proper selection of the metal is essential.

Fouling and poisoning are not the sole sources of catalyst deactivation, however. Severe restructuring, leaching, and even complete dissolution of the catalyst have been observed during long-term operation. Firstly, oxidic supports such as SiO_2 and Al_2O_3 , which are commonly used in refining and petrochemical processes, don't survive the hydrothermal and often acidic conditions applied in biomass conversion processes. One needs to resort to alternative support materials such as ZrO_2 , TiO_2 , or carbon. Degradation of the support is particularly critical when the reaction requires an acidic support because such a support and the acidic sites they carry are particularly prone to hydrolysis under hydrothermal conditions. Secondly, biomass conversion processes often require hydrogenation functions to saturate intermediates and/or remove oxygen from feed components. Cheap non-

precious metals generally suffer from leaching and/or sintering under hydrothermal conditions. The same applies to their compounds such as sulfides, carbides, nitrides, and phosphides. Hence, hydrogenation may require the use of expensive noble metals. Alternative and creative approaches are being explored to avoid or minimize the digestion of the catalyst support and its acidic or hydrogenation sites. Such approaches vary from making the catalyst more hydrophobic, for example, through coating with a carbon layer or anchoring alkane “fur”, or protecting it with an oxidic coating, for example, by atomic layer deposition.

Many of the challenges in terms of catalyst poisoning and destruction are related to the switch in the reaction medium from a hydrocarbon to water. However, other polar and coordinating media are also being explored for biomass conversion, for example, alcohol, polyols, carboxylic acids, and ionic liquids. Although specific deactivation challenges might occur in these media, their understanding will probably find a good basis in the principles discussed here.

The recognition of these stability challenges and of their importance for the industrial deployment of biomass conversion processes is a first and necessary step in the emergence of a robust bio-based economy. However, the journey has only just started. Much research is still needed to understand the deeper fundamentals of these challenges and develop creative and innovative approaches to mitigate the fouling, poisoning, and destruction of the catalyst. Mitigations will likely include the development of better and more robust catalysts. However, they will also require innovative approaches to process design through the development of, for example, new purification methods for the feed, new approaches to stabilize reactive feed components and reaction intermediates, new concepts to avoid contact of the fouling/poisoning/destroying agents with the catalyst, or novel routes for cheap and effective regeneration of the catalyst. The coming decades promise many exciting reports in these areas.

Appendix

The electronegativities of oxide additives were calculated as defined by J.-P. Jolivet.^[64] Accordingly, the electronegativity of a mixed oxide $\text{EN}(\text{MO}_x)$ is defined below using the Allred-Rochow scale for the electronegativity $\text{EN}(i)$ of elements i . For reference, water has an electronegativity of 2.5 [Eqs. (1) and (2)].

$$\text{EN}(\text{MO}_x) = \frac{\text{Angew. Chem. 2015, 127, 13382–13394}}{(\text{EN}(\text{M})^{0.5} + x \text{EN}(\text{O})^{0.5}) / (1/\text{EN}(\text{M})^{0.5} + x/\text{EN}(\text{O})^{0.5})} \quad (1)$$

$$\text{EN}(\text{M}(\text{OH})_x) = \frac{\text{Angew. Chem. 2015, 127, 13382–13394}}{(\text{EN}(\text{M})^{0.5} + x \text{EN}(\text{O})^{0.5} + x \text{EN}(\text{H})^{0.5}) / (1/\text{EN}(\text{M})^{0.5} + x/\text{EN}(\text{O})^{0.5} + x/\text{EN}(\text{H})^{0.5})} \quad (2)$$

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