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Green Catalysis by Nanoparticulate Catalysts developed for Flow Processing? Case Study of Glucose Hydrogenation

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Heterogeneous catalysis, flow chemistry, continuous processing, green solvents, catalyst immobilization and recycling are some of the most relevant, emerging key technologies to achieve green synthesis. [10] However, a quantification of potential effects on a case to case level is required to provide a profound answer, whether they can lead to a superior process compared to the industrial standard. To do so, holistic environmental assessment approaches are very useful tools providing insights and decision support already during the process development phase. Herein, novel heterogeneous nanoparticulate ruthenium catalysts immobilized on hyperbranched polystyrene (HPS) and nitrogen-doped carbon nanotubes [15] (NCNT) were investigated with respect to their potential environmental impacts and improvements if utilized in an industrially highly relevant process, namely glucose hydrogenation to sorbitol. The results of a comparative Life Cycle Assessment of the alternative catalytic systems under consideration of Raney nickel as benchmark catalyst revealed that in particular Ru nanoparticles on porous HPS beads processed under flow-chemistry conditions have the potential to improve the greenness of the overall synthesis, but [20] the concentration of glucose in the reaction mixture is in fact the most influential parameter.

Introduction

Sorbitol is a major specialty product and the polyol with the most widespread use in nutrition, cosmetics, medicine and industry[1] and [25] therefore represents a compound that is encountered in many everyday life utilities. Large amounts are used as alternative sweetener for diabetics, but it is also applied as humectant and binding agent in cosmetics or food, for example in toothpaste, where it not only prevents its dehydration but also contributes to its taste [30] and its non-cariogenic effect.[2] Additionally, sorbitol is a starting material for the industrial synthesis of vitamin C,[3] which in turn has various applications. The worldwide production volume exceeded 1,000,000 t/a in 2000.[1] Especially the growing demand in China[4] stimulates many sorbitol producers to increase their production. The [35] current selling price of sorbitol ranges between $ 0.95 and $ 1.40 per kg (70 % syrup).[5]

Sorbitol is mainly produced *via* catalytic hydrogenation of D-glucose – being an abundant and cheap feedstock derived from renewable resources.[1, 6] In industry, sorbitol production is typically based on [40] Raney nickel catalyzed slurry batch or sometimes fixed-bed continuous processes.[6, 7] In a first instance, the process mostly complies with the twelve principles of green chemistry[8], *e.g.*, high atom economy, use of renewable feedstocks, use of water and production of degradable and innocuous materials. However, the [45] following issues have led to a reconsideration of the manufacturing process within the last decade: i) the increasing demand for and the severe price competition on the sorbitol market, and ii) environmental and health concerns as well as high purification efforts due to the leaching of Raney nickel at hydrogenation [50] conditions.

Therefore, the development of continuous hydrogenation processes has been considered to a greater extend and alternative catalytically active transition metals have been tested in hydrogenation reactions. Even so, the improvement of the established process remains [55] challenging, as all of the following requirements have to be covered: i) selectivity and conversion need to be competitive (> 99 %); ii) the catalyst has to feature high stability and no leaching behaviour; iii) new ways of producing sorbitol have to not only be advantageous concerning handling and health aspects, but have also to be low in [60] costs and environmental impact.

These ideas for process improvement have been followed within the collaborative project POLYCAT. The acronym abbreviates 'Modern POLYmer-based CATalysts and microflow conditions as key elements of innovations in fine chemical syntheses'. The project was [65] launched by the European Community's Seventh Framework Programme. The aim is to develop an integrated, coherent and holistic approach utilizing novel heterogeneous nanoparticulate catalysts in vitamin, pharmaceutical and crop protection syntheses in conjunction with functions of microreaction technology and 'green' [70] solvents. Thus, process design activities within POLYCAT are accompanied by an iterative evaluation approach for most

environmentally benign and economic viable design alternatives.[9, 10] Decision making on different stages of development was supported by applying Life Cycle Assessment approaches in order to identify the best alternatives not only from a technical but also from an ecological perspective. In this context, also the stage of catalyst preparation and its influence on the greenness of redesigned or optimized processes played a crucial role (see also Figure 1).
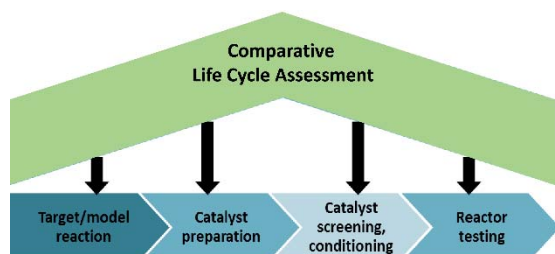

Figure 1: Overall evaluation approach during process design of modern nanoparticulate catalysts for hydrogenation reaction.

In this context, different alternatives in the development of a new way of catalytic hydrogenation reaction using heterogeneous nanoparticulate catalysts in flow-processing have been assessed. As mentioned above, the reaction of D-glucose converted to sorbitol is already conducted in industry at large scale. Thus, it is well suited to prove the potential greenness of modern nanoparticulate catalysts for hydrogenation reactions in food- or cosmetic industry.
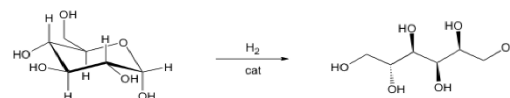
Background

D-Glucose Hydrogenation: State of the Art

Sorbitol can be produced from different sugars, but the synthesis from D-glucose results in the highest purity of the product and is therefore preferred. The most common manufacturing method is the catalytic hydrogenation using metallic catalysts. There are also microbiological processes known but these have not yet achieved an economic importance.[5, 11]

The catalytic hydrogenation of D-glucose to give sorbitol is depicted in Scheme 1. The reaction is conducted under elevated pressure and temperature conditions using a hydrogenation catalyst. Early patents starting from 1925 describe the hydrogenation with nickel or Raney nickel catalysts in a batch process.[3, 12-14] An amount of 2.5 to 12 %wt of the nickel catalyst is added to the D-glucose solution (usually 30 to 60 %wt). Hydrogen gas is added at excess pressure (> 100 bar) at temperatures between 100 to 170 °C. In many production sites, the procedure has remained unchanged. However, from the 1980s on, continuous processes were tested as well.[5] The continuous process is typically conducted under similar process conditions using sublimed or fixed-bed catalysts. If necessary, the catalyst is removed by precipitation and filtration. Afterwards the product mixture has to be decolorized (for example using activated charcoal) and nickel ions have to be removed to a level that is suitable for the area of application by using ion exchangers.

More recently the hydrogenation of D-glucose with ruthenium catalysts at industrial scale has been described.[15, 16] The process conditions are comparable to the ones described above, but the used amount of metal catalyst is typically smaller. However, to date industrial manufacture of sorbitol is still carried out in slurry reactors

using Raney nickel catalysts due to its low price and its high selectivity for sorbitol.[17] Leaching of nickel into the product causes a limitation of the number of reuses of the catalyst and requires an elaborate clean-up.[1]

Scheme 1: Reaction equation for the hydrogenation of D-glucose.

The advantages of using Ru as alternative catalyst are numerous: Ru does not dissolve under the reaction conditions of the D-glucose hydrogenation, and therefore does not cause any issues related to metal leaching. Thus the catalyst may remain active for a longer time and purification expenditures will be reduced. In addition, higher selectivities[15] and mass-specific activities were reported.[1, 6] Due to the expensive price of Ru, it is usually fixed on a support.

Novel Catalytic Systems focused within POLYCAT: Nanoparticulate Ruthenium based Catalysts

The present Life Cycle Assessment study is focused on the development of new, nanoparticulate Ru based catalysts on nanostructured supports catalyzing the hydrogenation of D-glucose. A major advantage of nanoparticles in catalysis is their large surface area that leads to a comparably high number of catalytic reactions at a time and therefore increases the catalytic activity.[18-22] A variety of reasons for the better performances of nanoparticulate catalysts has been discussed in recent literature: geometry, oxidation state, chemical and physical environment, interparticle interactions, nanoparticle – support interactions etc.[23]

Thus, the most important aspect in the development of nanoparticulate catalysts is control over nanoparticle size and morphology as well as prevention of their nanoparticulate aggregation and leaching during the reaction.[23, 24] Besides, low-cost, reproducible and scalable approaches to nanocatalyst synthesis are of great importance.[25] Among the diverse catalytic nanomaterials, supported metal nanoparticles are the most widely studied and extensively employed in many industrial processes.[25] The most prospective supports are nanostructured polymers (e.g., dendrimers, polymeric networks, etc.), which can serve as an organic macroligand for growing nanoparticles and are able to provide a solution for a number of the above-mentioned issues related to the use of nanoparticles in catalysis.

Within this study, hypercrosslinked polystyrene (HPS) and nitrogen-doped carbon nanotubes (NCNT) were investigated in detail. Both kinds of materials facilitate the stabilization of the metal nanoparticles on the surface, influencing e.g. catalyst lifetime and catalytic activities.[11] In the following, both systems as well as expected advantages justifying their application will be described in more detail.

Hyperbranched Polystyrene Supported Catalysts

HPS networks were first synthesized in the early 1980s by crosslinking linear polystyrene chains with bifunctional crosslinking agents like monochlorodimethylether or p-xylylen dichloride as shown in Figure 2a.[26] Originally used as sorbent material, HPS is

nowadays produced commercially by several companies.[27]

Due to its high crosslinking degree, which can exceed 100 %, the structure contains nanosized pores. During impregnation with a metal salt, nanoparticles are formed inside these pores where they can be kept stable. The unique feature of HPS is the ability to swell in different solvents[28] which favours the inclusion of various metal-containing compounds in the HPS matrix. Because of its large surface area, (usually specific surface area (SSA) > 1,000 m²/g), its thermal stability (up to 300° C)[29] and its well-defined interfaces HPS is very suitable for the application as support material for metal nanoparticles in catalysis.[30, 31] Figure 2b symbolizes the expected structure of the nanoparticles in the nanopores of an HPS-bead. X-ray photoelectron spectroscopy analyses revealed that the Ru nanoparticles have a mixed structure (their surface is partially reduced to Ru(0)). Based on a kinetic study, Doluda et al. proposed that both Ru(0) and Ru(IV) oxide on the nanoparticle surface are responsible for catalytic hydrogenation for different reason, i.e. Ru(0) participates in hydrogen activation while Ru(IV) – in D-glucose adsorption.[32]
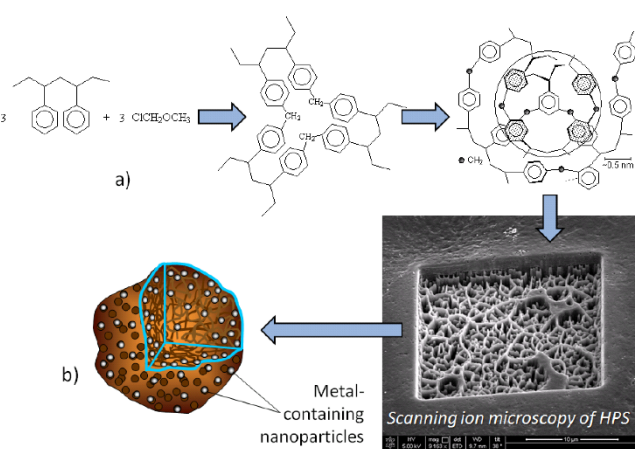

Figure 2: Scheme of HPS synthesis (a) and nanoparticle formation in the nanopores of a HPS-bead (b).

CNT / NCNT Supported Catalysts

The synthesis of Carbon Nanotubes (CNT) was first described in 1991 by Iijima.[33] His investigations indicated outstanding characteristics: The material is stronger than steel, harder than diamond, its electrical conductivity is higher than that of copper, its thermal conductivity is higher than that of diamond, to mention but a few.[33, 34] Furthermore, carbon nanotubes are an interesting support material for metallic nanoparticulate catalysts because of their unique electronic and morphological properties. There is a strong electronic interaction between the CNT support material and the catalytically active metal, which results in a strong adhesion and a promotion of the catalytic activity. The shape of the tubes allows a good accessibility for the substrate to the catalytically active metal and good transportation properties.[35, 36] Doping the CNT with N-atoms leads to an additional functionality for the attachment of the nanoparticles.

Both CNT and nitrogen-doped carbon nanotubes (NCNT) are usually synthesized by chemical vapour deposition (CVD).[37] Depending on the desired composition of the nanotubes, the precursor can contain nitrogen atoms, which leads to the formation of NCNT. Figure 3 shows a magnified image of NCNTs. The utilization of NCNT based ruthenium catalysts within the hydrogenation of glucose is advantageous compared to the use of Ru/C, which was done before,[6] as Ru/NCNT has a higher mechanical stability, porosity and therefore a higher accessible surface area.
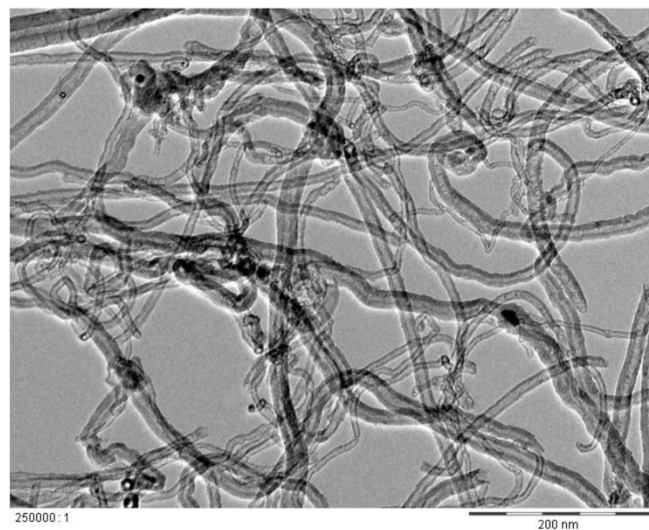

Figure 3: Depiction of NCNTs by means of transmission electron microscopy.

LCA-Modelling

In order to support the process design efforts for modern catalytic pathways for glucose hydrogenation, a comparative environmental assessment and holistic decision making procedure was followed consistent with previous studies, see, e.g., references.[38-40] The LCA methodology [41, 42] was chosen to quantify and assess the potential environmental impacts associated with the alternative catalytic systems under investigation. During iterative evaluation steps, the information about environmental impact criteria is used for process improvement. Key aspects for green process improvement are determined and then taken into account within the next iterative step of process design. The evaluation is refined and narrowed down in parallel to the process development activities. At the end, the environmental impacts of the new process design alternatives are quantified and compared with a benchmark process.

The outcome of experimental investigations on D-glucose hydrogenation served as database for the Life Cycle Inventory (LCI). As ruthenium is a dependent co-product of the platinum group metal (PGM), the extraction of the primary metal from the ore as well as the pyrometallurgical processing and hydrometallurgical purification in case of the secondary (recycled) metal was modelled based on LCI data referred to the PGM group. Information on detailed LCI gathering regarding catalyst preparations can be found in the appendix. In case of low data availability the LCI analysis approach introduced by Hischier et al.[43] was followed, allowing the integration of average values regarding transportation of goods[45], energy and water consumption[46] and plant infrastructure. In general, process waste was considered to be disposed via hazardous waste incineration. Waste water was considered to be disposed via waste water treatment. More information about the data quality can be

found in ESI Table 1 - 4.†

LCI analysis and Life Cycle Impact Assessment (LCIA) were supported by the software tools Umberto® NXT LCA[47] and the LCI database Ecoinvent v.3.0.[44] LCIA was conducted applying the LCIA
[5] methodology "ReCiPe 2008" by Goedkoop et al.[48] The following ReCiPe environmental impact potentials were considered: Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Terrestrial Acidification Potential (TAP), Freshwater Eutrophication Potential (FEP), Human Toxicity Potential (HTP), Photochemical
[10] Oxidant Formation Potential (POFP), Terrestrial Ecotoxicity Potential (TETP), Natural Land Transformation Potential (NLTP), Metal Depletion Potential (MDP) and Fossil Fuel Depletion Potential (FDP). They were addressed at the midpoint level and 'hierarchist' perspective. This perspective is in accordance to the
[15] most common policy principles with regard to time-frame and other issues.[49] Most frequently, the 100 year timeframe was used. The LCIA results presented in the following are based on the functional unit FU = 1 kg sorbitol.

The LCIA categories GWP and MDP were selected for screening
[20] purposes. On the one hand, anthropogenic greenhouse gas emissions are one of the most urgent global environmental problems and are directly related to energy intensive process steps, thus particularly awakening stakeholder's interests. On the other hand, MDP accounts for the consumption of the finite source of metals that cannot be
[25] substituted for future generations. It is an important factor to be considered when creating green catalytic processes.

The production processes were subdivided in five process steps: The support preparation (HPS, NCNT), the catalyst preparation (HPS/Ru, NCNT/Ru, Raney nickel), the D-glucose hydrogenation
[30] and the vaporization of the product solution in order to give 1 kg of

50 %wt sorbitol solutions and a clean-up process (only in case of the Raney nickel catalyzed process). These processes were defined as integral parts of the system boundary of this LCA study.

Benchmark Process

[35] The today's practice of industrial catalytic hydrogenation of D-glucose to sorbitol was used as a benchmark process. It is described in numerous literature sources. However, none of the procedures in literature described the entire process in such a way that it could be used to perform LCA. Therefore, process parameters
[40] were selected combining the information given in several literature sources.[3, 5, 12-14, 45] For the calculation of the potential environmental impacts of the benchmark process the following assumptions concerning the reaction conditions are made: The reaction is carried out in batch mode with an amount of catalyst of 2 g per kg D-glucose,
[45] the D-glucose concentration is 50 %wt (5.6 M), the temperature 110°C, hydrogen pressure 40 bar, and the reaction time is 3 h. The clean-up is performed with a polymer-based ion exchanger. The lifetime is assumed to be three years, 2 M HCl serves as regeneration agent.

[50] **Process Alternatives in Focus**

The process conditions investigated for batch and continuous, polymer supported ruthenium catalyzed hydrogenation alternatives as well as benchmark process are summarized in tables 1 and 2. For interested readers, more detailed information can be found in chapter
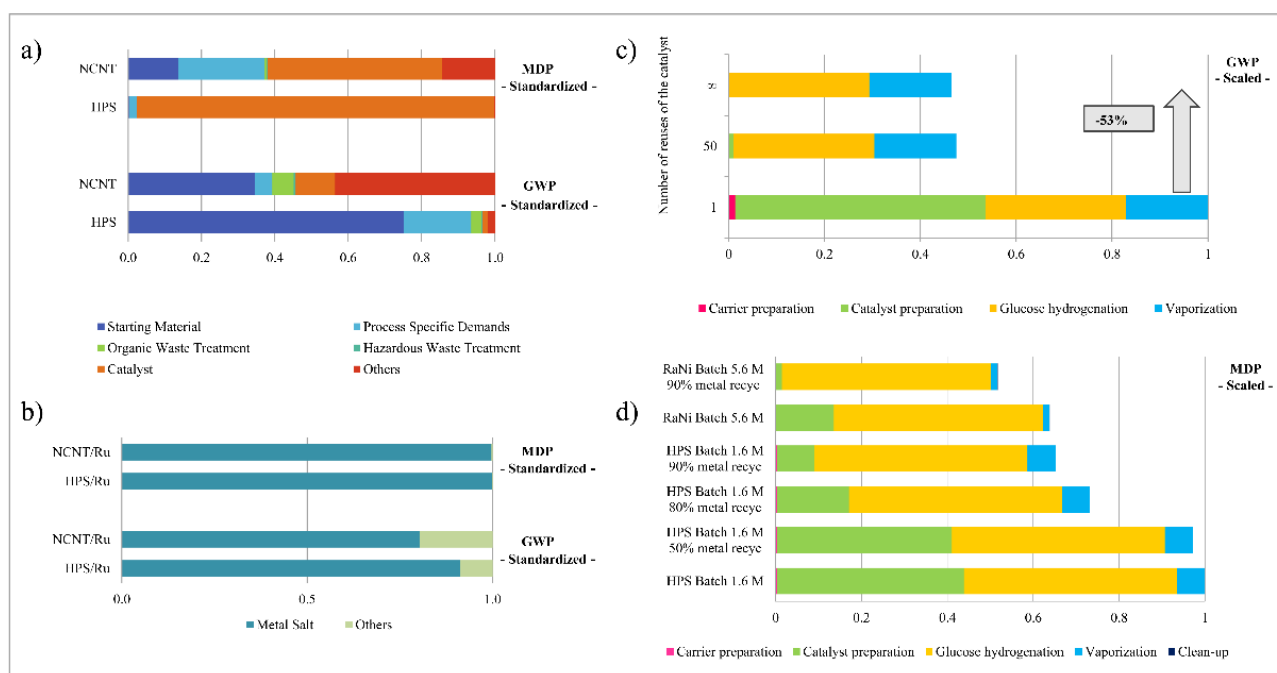[55] "Materials and Methods".

Figure 4: Potential environmental impacts (scaled to 1 and worst case scenario, respectively) of a) preparation of the polymer-based support material hyperbranched polystyrene (HPS) and nitrogen-doped carbon nanotubes (NCNT) with regard to GWP and MDP; b) impregnation of the supports to give the two hydrogenation catalysts HPS/Ru and NCNT/Ru with regard to GWP and MDP; c) glucose hydrogenation (scenario: *HPS Batch 1.6*) in dependence of catalyst cycles: 1, 50, ∞, exemplarily shown for GWP; d) Ru catalyst recycling and reuse (0 – 90 %) with regard to MDP (for the example of scenario *HPS Batch 1.6 M* referred to benchmark *RaNi Batch 5.6 M and RaNi Batch 5.6 M 90 % metal recycling*).

Table 1: Conditions of the glucose hydrogenation process alternatives under investigation in laboratory scale used for the LCA.

Scenario	Batch Processes		Continuous Processes	
	HPS Batch 1.6 M	NCNT Batch 0.1 M	HPS Conti 0.5 M	NCNT Conti 0.2 M
Catalyst [%wt Ru]	3.0	3.6	2.85	2.2
Catalyst/ glucose ratio [g/kg]	0.56	1.39	0.02	0.60
TOF [mol sorbitol/ mol Ru*h]	218	85	2,535	376
Conversion [%]	98	96	99.3	91
Selectivity [%]	99	97	99	98

* at T > 100°C

Table 2: Theoretical scenarios – industrial application of glucose hydrogenation process alternatives used for the LCA.

Scenario	Batch Processes		Continuous Processes		Benchmark
	HPS Batch 5.6 M	NCNT Batch 5.6 M	HPS Conti 5.6 M	NCNT Conti 5.6 M	RaNi Batch 5.6 M
Catalyst [%wt Ru]	3.0	3.6	2.85	2.2	-
Catalyst/ glucose ratio [g/kg]	0.56	1.39	0.02	0.53	1.98
TOF [mol sorbitol/ mol cat.*h]	218	85	2,535	376	132
Conversion [%]	97	95	99	80	98

* at T > 100°C

First of all, the evaluation studies were focused on lab scale process options (batch and continuous mode) using the novel developed catalyst systems to identify bottlenecks and improvement potentials to be considered for a later pilot or industrial scale implementation. The conditions described were chosen according to experimental investigations (firstly, without any optimization, *i.e.* base cases, see table 1). After these optimization studies, the environmental performances of future batch and continuous processes were compared to the industrial benchmark process using Raney nickel (see table 2). On the one hand, these scenarios indicate a potential up-scale of the most promising, technically feasible experimental scenarios. On the other hand, these options describe potential, hypothetical ones to investigate parameters guaranteeing competitiveness to the industrial benchmark process.

Results and Discussion

Environmental Impacts along the Manufacturing Process Chains and Utilization of Nanostructured Catalytic Systems

Before evaluating the performance of the catalysts in the hydrogenation reaction, the Life Cycle Impact potentials of the alternative batch catalytic systems themselves were investigated in detail. Figure 4a depicts the results of the investigation of the environmental impacts of the support materials HPS and NCNT by means of two representative LCIA categories, GWP and MDP. It

becomes obvious that for both production processes, GWP is mainly influenced by the consumption of the feedstocks styrene (in case of HPS B*atch 1.6 M* (75 %)) and acetonitrile (in case of NCNT *Batch 0.1 M* (35 %)). Further, both materials are produced by applying a catalyst. In both cases the impact of these catalysts on GWP is marginal, however, their supply dominates the category MDP: The tin salt used for the HPS production[26] causes 97 % of the overall MDP. For the NCNT-production the catalyst made from numerous metal salts[35] causes 48 % of the total MDP (figure 4a). In figure 4b the impacts of the impregnation step, giving the final hydrogenation catalysts HPS/Ru and NCNT/Ru, is visualized. Obviously, the largest share of the potential impacts results from the consumption of the Ru salt used for the precursor solution. *This clear result can be observed for numerous other LCIA categories as well and emphasizes the importance of a thoughtful consumption of this metal and/or metal recovery from waste streams.* To give an example, the overall MDP would drop by 30 %, if the ruthenium loss during the preparation of the polymer-based catalytic HPS/Ru (3.0 %wt. Ru) system is decreased to 0 % compared to currently 47 %. For the NCNT-based system (3.6 %wt.), a reduction from 32 % Ru loss to 0 % results in a decrease of the MDP to 45 % of the initial value. Figure 4c, which puts the production of the catalyst in the context of its application in D-glucose hydrogenation and downstream chains, points out the strong dependency of the environmental impact potentials on the catalyst lifetime. The GWP for example could be reduced by 53 % when reusing the catalyst endlessly instead of exchanging it after every run. *To give a better impression, a catalyst reuse number of 50 can be taken as a rough value clearly outweighing environmental burdens resulting from the catalyst manufacturing.*

Besides the option of catalyst reuse, the use of secondary materials instead of primary raw materials is an important key issue for sustainability. In figure 4d, the influence of the application of secondary ruthenium or Raney nickel on the resulting MDP of the overall D-glucose hydrogenation process is exemplarily shown by means of the scenario *HPS Batch 1.6 M* compared to the benchmark *RaNi Batch 5.6*. The MDP of recycled catalytic material is lower by two orders of magnitude improving the environmental performance to a great extent. *It was calculated that the share of recycled metal compared to the overall metal consumption used for the impregnation of the support has to be around 88 % in order to reduce the impact of this scenario even down to the level of the RaNi Batch 5.6 process* calculated assuming primary metals. It becomes impressively obvious that long-term stability and reusability of the newly developed catalysts are essential requirements for the greenness of the overall process.

View for the Whole: Key Criteria for Green D-Glucose Hydrogenation Process in Batch

Next, the investigations were extended by further LCIA impact categories to guarantee a more holistic decision making towards green process design options. Thus, fingerprint analyses of the key environmental impacts of the existing batch procedures for D-glucose hydrogenation were performed (Figures 5 and 6). Figure 5 shows that in case of the *HPS Batch 1.6 M* scenario three main aspects of the reaction dominate the potential environmental impacts. The environmental impacts in a number of categories are mainly caused by the supply of the feedstock D-glucose. It causes for example 87 % of the TETP. In the categories MDP and TAP the main

contribution (60 %) is caused by the supply of the catalyst. The vaporization step causes significant impacts in several categories (up to 37 % in the category HTP).
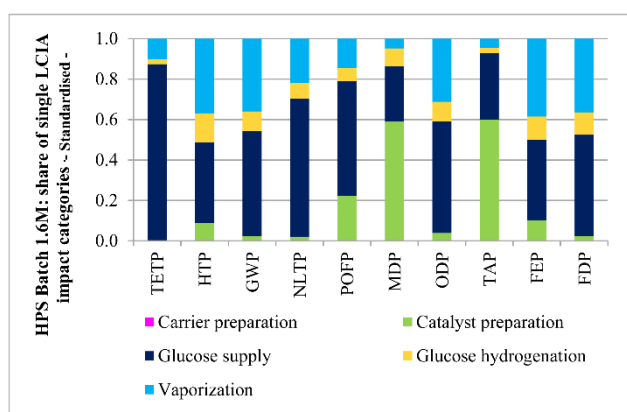

Figure 5: Fingerprint analysis for the base case (*HPS Batch 1.6 M*) of the HPS-based glucose hydrogenation.
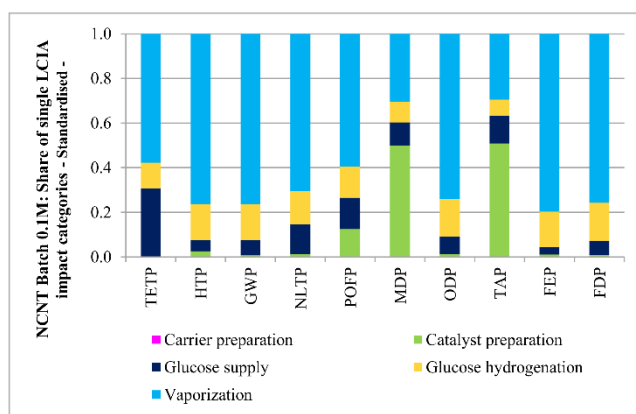

Figure 6: Fingerprint analysis for the NCNT base case (*NCNT Batch 0.1 M*).

Transfer from Batch to Continuous Processing: Prognosis and Actions to be taken

Taking the above key criteria into account, hypothetical scenarios were defined (see Table 2) allowing a first glance on their environmental competitiveness to the industrial benchmark process, see Figure 7.

The LCIA fingerprint of the *NCNT Batch* scenario (Figure 6) revealed the following: i) almost all impact categories are dominated by the vaporization step (up to 80 % in the category FEP), which is a result of the low glucose concentration employed; ii) The share of the impact of the D-glucose hydrogenation is higher than in the HPS-based process (up to 17 % in the category FDP); iii) The dominating contribution of the catalyst in the categories MDP and TAP (50 %) is comparable to the HPS-based process.

By means of these insights, the key criteria for process improvements were defined as follows: i) energy intensive processes such as the heating and vaporizing of the solvent water contribute largely to the potential environmental impacts in many categories. The development of a catalyst that works at a high concentration, such as 30 to 50 %wt. as described in references [12-15, 45], is favourable; ii)

the environmental impact of the catalyst used should be minimized by means of reduced metal load and/or the application of recycled material; iii) high conversion rates and selectivities are also important for a positive environmental performance, since the agricultural supply of the raw material D-glucose has a relevant share on the overall environmental impact.

The experimental transformation from batch to continuous processing applying both catalytic systems enabled the reduction of the D-glucose / catalyst ratio to 4 % (HPS) and 43 % (NCNT) of the batch ratio. However, the process changes led to a decrease of the conversion from 95 % to 89 % in case of the NCNT-based catalytic system. Under laboratory scale conditions, low concentrated aqueous substrate solutions and primary ruthenium for catalyst preparation were used (Table 1). In order to estimate the effect of an increase of the concentration of the feed solution to 50 %wt, likely in industrial practice, some theoretical scenarios were calculated as well. Additionally, a theoretical recycling scenario was investigated. A ratio of secondary ruthenium being 3/4 of the overall ruthenium demand was considered for the example of the NCNT-based catalytic system (Figure 7).
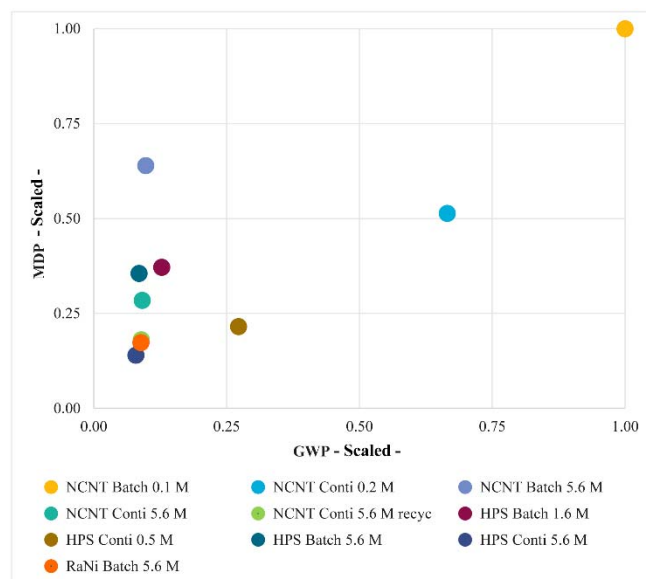

Figure 7: Assessment of alternative catalytic process scenarios compared to benchmark regarding GWP and MDP.

In both experimentally investigated continuous process alternatives the amount of catalyst per kg of D-glucose was reduced, as an exchange of the catalyst was not required as often as in the batch process. In addition, the amount of ruthenium on the support was decreased. Therefore the MDP is decreased by around 42 % in case of the *HPS Conti 0.5 M* scenario.

If furthermore a common concentration for the industrial D-glucose hydrogenation is assumed as done in the theoretical scenarios (Table 2), *HPS Batch 5.6 M* and *HPS Conti 5.6 M*, the GWP would be in a competitive range compared to the industrial benchmark process *RaNi Batch 5.6 M*. As the HPS batch process has already been conducted at a higher substrate concentration, chances are good, that the theoretical scenario *HPS Conti 5.6 M* which ranges in the same magnitude of impact in both categories as the Raney nickel

benchmark process does, can be practically put into realization.

The same consideration was made for the NCNT-based system: The performance of the catalyst of the original batch process was improved in the continuous process by decreasing the amount of catalyst used and decreasing the amount of metal impregnated on the support. This way, the MDP was decreased by about 44 %. As the concentration in the first batch experiments was lower, the increase of the concentration also contributes to the improvement of the GWP by around 1/4.
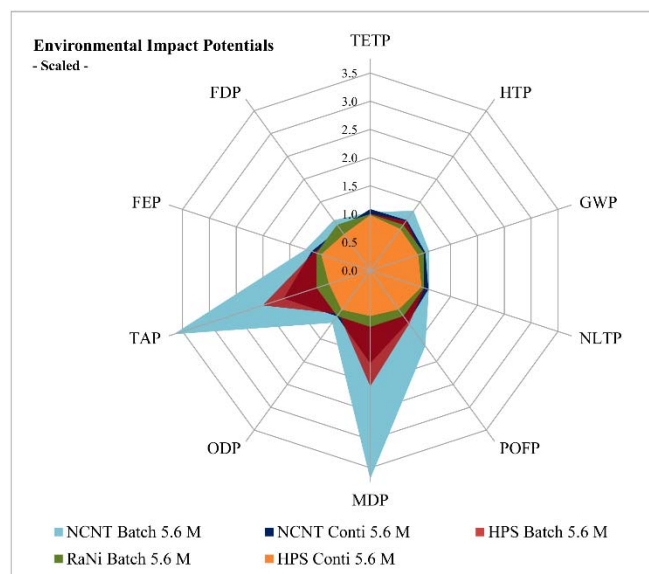

Figure 8: Comparison of environmental impact potentials of glucose hydrogenation process alternatives referred to benchmark RaNi Batch 5.6 M - Constraint: high concentrated reaction mixtures.
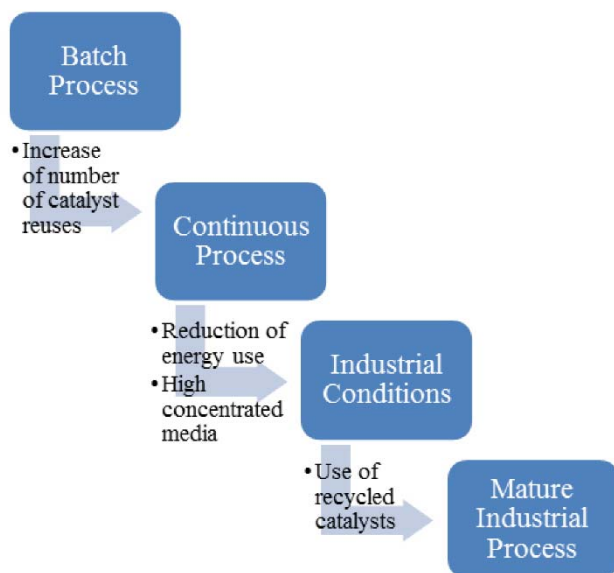

Figure 9: Measures to decrease the environmental burdens caused by the glucose hydrogenation catalyzed by NCNT/Ru and HPS/Ru. They are put in an order of priority in which they should be pursued.

The increase of the concentration to an industrial level as done in the theoretical scenarios NCNT Batch 5.6 M and NCNT Conti 5.6 M will decrease the environmental burdens further, so that the GWP can be reduced to 1/10 of the original value and has then a comparable environmental impact to the impact of the Raney nickel process. Unfortunately, the MDP would be still larger than for the RaNi Batch 5.6 benchmark process.

Interestingly, the environmental impact caused by the additional Ni separation step required in case of the conventional process were found less influential than expected.

Finally, the learnings gained by means of the exemplarily evaluation of the impact categories GWP and MDP were proven by the holistic assessment of ten of the categories considered by the ReCiPe midpoint LCIA. The results are shown in Figure 8. *They underline the positive effect of the transfer of sorbitol production from batch to continuous processing. They also support the findings resulting from the analysis of GWP and MDP that HPS/Ru may become a superior catalytic system for hydrogenation reactions compared to Raney nickel.*

Conclusion and Outlook

Within this comparative LCA study, the utilization of novel heterogeneous, nanoparticulate catalytic systems for hydrogenation reactions were critically evaluated against the state of the art by means of a reaction of high industrial relevance. With both newly developed systems, catalyst leaching into the product sorbitol can be totally avoided, whereas activity and selectivity can be kept high over time.

The results confirmed that the polymer-based nanoparticulate catalyst HPS/Ru will be able to compete with the industrial benchmark catalyst Raney nickel in the hydrogenation of D-glucose, if the reaction can be performed also under industrial reaction conditions in a continuously running process utilizing highly concentrated D-glucose solution. In contrast, the industrial scale use of NCNT/Ru for sorbitol production was forecasted to be less competitive, being due to lower substrate concentrations, conversion and higher catalyst/glucose ratio. However, this outcome may depend on the current state of development of both systems under laboratory scale conditions and can vary after further optimisation and scale up.

According to the findings, a strategy was developed to compete with the classical sugar hydrogenation procedure. The overall strategy in order to decrease the environmental burdens caused by the D-glucose hydrogenation catalyzed by NCNT/Ru or HPS/Ru is depicted in Figure 9 in an order of priority in which they should be pursued. Although the process *per se* seemed to be green at a first glance, several hot spots occurred during the development process accompanied by a detailed evaluation of all process chains which emphasizes the need for a more critical and holistic evaluation of catalytic processes. Thus, as an example, although the catalyst is used in marginal amounts, its environmental impact is indeed significant. Further, water – often implied as a green solvent – maybe no longer green if energy-intensive separation steps becomes necessary.

At the current stage of development, a combination of the LCA study with a full Life Cycle Costing analysis was not realizable, since too many uncertainties and inconsistencies in the data especially

concerning material costs remained. However, first cost estimations revealed some hints concerning hot-spots and improvement potentials:

The costs for the HPS catalyst preparation are mainly caused by the high costs of ruthenium salt and labour costs. Nevertheless, the prices of the HPS-based catalyst and the Raney-Nickel benchmark are in a comparable range. The same insight could be gained for the glucose hydrogenation process under application of the HPS based catalyst. Here, we also found the costs for labour to exceed the other cost aspects by far, yet. This will surely substantially decrease in parallel to a process scale-up. In case of the NCNT-based catalyst, the NCNT support itself currently cause a major price difference when comparing only the three catalysts. Due to this and due to the comparatively high use and heating of water, the cost estimation of NCNT-based glucose hydrogenation showed that this process needs some more process optimization steps in order to be competitive.

All in all, the results indicated that a switch from batch to continuous processing utilizing novel nanoparticulate HPS/Ru catalysts can pave the way to a more efficient sorbitol production, but further investigations under pilot-scale conditions need to reveal whether the new catalyst alternatives stand the reaction conditions of the industrial established process. NCNT/Ru based catalysts will even need more development time and efforts to become a green and cost efficient catalyst for sugar hydrogenation.

Abbreviations

CNT	carbon nanotubes
CVD	chemical vapour deposition
FDP	fossil fuel depletion potential
FEP	freshwater eutrophication potential
GWP	global warming potential
HPS	hypercrosslinked polystyrene
HPLC	high pressure liquid chromatography
HTP	human toxicity potential
LCA	life cycle assessment
LCI	life cycle inventory
LCIA	life cycle impact assessment
MDP	metal depletion potential
NCNT	nitrogen-doped carbon nanotubes
NLTP	natural land transformation potential
ODP	ozone depletion potential
POFP	photochemical oxidant formation potential
RaNi	Raney nickel
SSA	Specific surface area
TAP	terrestrial acidification potential
TETP	terrestrial ecotoxicity potential

Acknowledgement

Appendix: Detailed description of the experimental procedures

In the following, the experimental procedures of catalyst preparation and D-glucose hydrogenation, being the basis of LCI analysis, are given.

Preparation of Nanoparticulate Catalytic Systems on Nanostructured Supports

HPS/Ru. The Ru-containing HPS-based catalysts (designed as HPS/Ru) were synthesized according to the procedure described elsewhere.[46] In a typical laboratory-scale experiment, 3 g of the support material HPS (purchased from Purolite Int., United Kingdom, as Macronet MN100) was washed with water and dried under vacuum (moisture < 2 %). The procedure for the production of the HPS material published in detail in Tsyurupa et al..[26] Then the support was impregnated with 8 mL of ruthenium catalyst precursor solution, which was prepared in a separate vessel from tetrahydrofurane (6 mL), methanol (1 mL), water (1 mL) and $Ru(OH)Cl_3$ (0.39 g). This solution was mixed for 20 min, before it was added to the HPS material. Impregnation was carried out by continuous stirring during 10 min. After the impregnation the catalyst was dried at 70 °C and boiled with 0.1 M sodium hydroxide with the addition of hydrogen peroxide (30 %) for about 2 h. Such a treatment induced the formation of RuO_2 nanoparticles inside the pores of the HPS matrix. Afterwards, the catalysts containing RuO_2 nanoparticles were separated from this solution by filtration, washed with water and dried at 70 °C. Before testing the obtained catalysts in D-glucose hydrogenation they were reduced in hydrogen flow at 300 °C and ambient pressure during 2 h. The treatment resulted in nanoparticles with mixed valence structure Ru(0) and Ru(IV).[46] Two types of HPS-based catalysts were synthesized: i) powdered HPS with a support particle size of less than 63 μm (for batch process), and ii) as-received HPS with the size of granules varying from < 0.3 mm (1 %) up to < 0.8 mm (90 %) (in case of continuous hydrogenation). The content of Ru in the catalysts is 3.0 %wt (batch process experiments) and 2.85 %wt (continuous experiments) according to the results of elemental analysis. Transmission electron microscopy pictures of the Ru/HPS catalysts can be found in Doluda et al..[32]

NCNT/Ru. A precursor solution was prepared from 0.610 g $RuCl_3*xH_2O$ (41 %wt Ru) and 250 mL deionized water, to which 4.75 g NCNT were added. The latter had been prepared as reported elsewhere[36] and consists of agglomerates containing particles sizes between 100 μm and 800 μm and a maximum in the particle size distribution at 355 μm. 150 mL of a 30 % aqueous solution of H_2O_2 were then added drop wise and under stirring keeping T ≤ 60 °C. After complete addition, the mixture was heated to 80 °C for further 3 h. The overall procedure took 5 h. The impregnated catalyst was filtered , washed, and dried in an oven at T = 100 °C The amount of water for the washing was on average 50 mL per 1 g of NCNT/Ru. The loading of Ru in the final catalyst used in batch experiments is 3.6 %wt. For all continuous D-glucose hydrogenation experiments, a similar catalyst containing 2.2 %wt Ru was employed. The size of the nanoparticles were found to be in the range of 1.38 ± 0.35 nm. More information about particle sizes and transmission electron microscopy pictures have been reported in Aho et al..[47, 48]

D-Glucose Hydrogenation

Hydrogenation of D-Glucose using HPS/Ru.

Batch Process. Hydrogenation of D-glucose to sorbitol was carried

out in a house made isothermal stainless steel batch reactor (120 mL) installed in a shaker according to a procedure described elsewhere.[46] The following reaction conditions were applied: temperature 140 °C, hydrogen pressure 40 bar, initial concentration of D-glucose 1.6 M, catalyst loading 0.4 g. Samples of the reaction mixture were analysed *via* High Pressure Liquid Chromatography (HPLC) complex UltiMate 3000 equipped with the comparison refractometer detector Waters 410.

Continuous Process. Hydrogenation was carried out in a tubular mini-fixed-bed reactor setup with an inner volume of 150 mL equipped with a tank containing the solution of D-glucose, tanks with hydrogen and nitrogen, flowmeter, temperature and pressure controllers, plate heat-exchanger and thermostat. The catalyst loading was 2 g. The reaction was carried out under the following conditions: D-glucose concentration 0.5 M, temperature 110 °C, hydrogen pressure 40 bar, glucose solution flow rate 19 mL/min. Samples of the reaction mixture were analysed as described for the batch process.

Hydrogenation of D-Glucose using NCNT/Ru.

Batch Process. Hydrogenation of D-glucose over NCNT/Ru was investigated in a Parr 4561 autoclave (300 mL). The autoclave was equipped with a gas entrainment impeller, baffles, heating jacket and a cooling coil, sampling line, pressure, temperature and stirring rate controllers. The D-glucose solution was pre-heated and saturated with hydrogen in a separate chamber. The catalyst sample was put in the reactor which was flushed with nitrogen and hydrogen before heating. When the reactor reached the desired temperature of 120°C the D-glucose solution was fed to the reactor and the total pressure was increased to 20 bars of hydrogen. Samples (1-2 mL) were periodically withdrawn through a 0.5 μm sinter during the experiments. A 0.1 mol/L 120 mL D-glucose (Fluka, ≥ 98 % purity) solution was used. The stirring rate was 1000 rpm. The experiments were carried out between 120 and 180 minutes and the amount of catalyst was between 0.1 and 0.2 g.

The concentrations of D-glucose and sorbitol were determined by HPLC (HITACHI Chromaster HPLC) equipped with a refractive index detector. A Biorad HPX-87C carbohydrate column was used, the mobile phase was 1.2 mM $CaSO_4$. The temperature of the column was 70 °C and the flow rate of the mobile phase 0.5 mL/min, the detector was at 40 °C. Calibrations were made for D-glucose and sorbitol.

Continuous Process. Continuous hydrogenation of D-glucose over NCNT/Ru was investigated in a continuously operating fixed bed reactor set-up having six reactors in parallel, operated in co-current trickle flow. The inner diameter of the reactor tubes was 12.5 mm and the length of the electrically heated part was 12 cm. K-type thermocouples were used to control the temperature. Knauer Smartline 100 pumps were used to feed the D-glucose solution (Fluka, > 98%). The reaction conditions used for the continuous set-up are the following: temperature 130 °C, glucose solution flow rate 2.0 mL/min, hydrogen flow rate 50 mL/min at a pressure of 20 bar. The glucose concentration was 0.2 mol/L and the amount of catalyst was 0.05-0.50 g. The particle size of the catalysts used in the continuous reactors were between 125 and 250 μm. Samples were periodically withdrawn from the reactors and analysed with HPLC as described in the previous section.

Further synthesis conditions for both, batch and continuous hydrogenation are summarized in Tables 1 and 2.

Notes

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