



Editorial

Hydrogenation and Dehydrogenation of Liquid Organic Hydrogen Carriers: A New Opportunity for Carbon-Based Catalysts

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The development of a hydrogen-based economy is the perfect nexus between the need of discontinuing the use of fossil fuels (trying to mitigate climate change), the development of a system based on renewable energy (with the use of hydrogen allowing us to buffer the discontinuities produced in this generation) and the achievement of a local-based robust energy supply system [1]. However, extending the use of hydrogen as an energy vector must still overcome challenging issues, with the key issues being related to its storage. Cryogenic or pressurized storage is relatively expensive, technically complex, and presents important safety concerns. As a promising alternative, the use of organic hydrogen carriers has been suggested in recent years. The ideal carrier will be an organic compound with a low melting point and low viscosity, with a significant number of unsaturated carbon–carbon bonds, in addition to being easy to hydrogenate and dehydrogenate. These properties allow us to store and transport hydrogen in infrastructures designed for liquid fuels, thus facilitating the replacement of fossil fuels by hydrogen [2].

The viability of LOHC-based hydrogen storage technologies relies on both in the selection of an organic with the desired properties (melting point below 30 °C, boiling point ideally higher than 300 °C, hydrogen storage capacity higher than 6% wt., low dehydrogenation enthalpy, high chemical stability in thermal cycles [2,3] and in the development of active and selective catalysts for the hydrogenation and dehydrogenation steps.

From the point of view of the chemicals involved, most of the organic compounds used up to now for this purpose (alkyl-carbazoles, dibenzyltoluene, etc.) are expensive, toxic and/or difficult to synthesize, being prepared from non-renewable carbon sources [4]. One of the key ideas at this point is trying to develop LOHC based on renewable resources. Thus, furanic aldehydes derived from the hydrolysis and dehydration of cellulosic biomass have been proposed as a hydrogen carriers. The first work reported in this issue was published by Verevkin et al., and demonstrates that furfuryl alcohol can be a useful hydrogen carrier [5]. At this point, the condensation of these furanic compounds (for example aldol condensation using acetone as linking molecule) leads to larger molecules with the highest hydrogen storage capacity. The hydrogenation behavior of these materials was studied, and it was concluded that it is possible to hydrogenate these compounds while maintaining the organic structure [6]. Another sustainable alternative for this purpose is the use of polyaromatic compounds obtained by Diel–Alders reactions from furanic molecules and alcohols of renewable origin. Molecules such as indenenes or naphthalenes can be obtained by biomass catalytic pyrolysis, the design of tailored catalysts for increasing the selectivity for these chemicals still being a matter of intensive research [7,8].

Once the LOHC molecule is selected, the next issue to be considered is the catalyst selection. It should be noted that the application of the LOHC technology involves two different catalytic reactions: hydrogenation of the carrier, saturating the multiple C–C bonds, and dehydrogenation, releasing hydrogen and regenerating the carrier. From the reactor engineering point of view, both processes can be performed at very different scales. Hydrogenation of the carrier will be performed at the site where hydrogen is generated.



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According to the suggested hydrogen generation routes, this will be close to renewable-powered water electrolyzers for hydrogen production (electrolytic green hydrogen) or methane reforming plants (blue hydrogen or non-electrolytic green hydrogen). In both cases, the configuration could be the usual one for petrochemical industries, mainly catalytic fixed bed, or triphasic configurations (trickle-bed, slurry reactor). In the same way, the hydrogenation technology itself is not absolutely new, as it is possible to apply all the background of industrial hydrogenations (for example from petrochemical industries) to these processes.

Nevertheless, there are significant differences that must be taken into account. The most important is the need for total conversion and total selectivity to the fully hydrogenated specimen, which requires higher catalyst loading than the petrochemical counterparts. The other distinctive feature is that this hydrogenation takes place at solvent-less conditions, with a large hydrogen demand. Thus, gas–liquid hydrogen mass transfer can be a controlling step of this process. Therefore, LOHC hydrogenation reactors design can be limited by mechanical and materials engineering aspects, as the maximum pressure allowable.

In the case of the dehydrogenation step, the variability of the proposed devices is largely wider. Depending on the application, small and intensified devices will be used (for example, when using hydrogen for transportation applications) or larger reactors, of analogous size to the hydrogenation reactors, will be used. In the first case, the minimal volume of the reactor will be the critical point, the development of microreactors being the most promising strategy for performing these reactions.

Unlike hydrogenation reactions, the background about industrial-scale dehydrogenation reactions is lower and mainly related to light hydrocarbons (ethane, propane, aromatization reactions), with important technical complexities to be solved. The first problem is the intrinsic endothermicity of this reaction (hydrogenation is slightly exothermic). This fact limits the size of catalytic fixed bed reactor, but also opens up new approaches involving integrations with other processes, such as the highly exothermic hydrogen combustion in solid oxide fuels [2]. The other specific technical issue of dehydrogenation reactors deals with the large amount of hydrogen generated within the reactor (two to three orders of magnitude larger than the volume of charged LOHC processed). This effect can lead to by-pass effects and decrease the space–time of the LOHC in the reactor, leading to incomplete conversions with lower hydrogen yields and a deficient regeneration of the hydrogen carrier. Advanced reactors, as radial flow reactors, spray-pulsed reactors or monoliths have been proposed to overcome this problem [2].

Concerning the catalytic materials, a plethora of catalysts has been suggested for both hydrogenation and dehydrogenation steps, depending on the selected LOHC. Catalysis plays a key role in hydrogen storage using LOHC systems, both for hydrogenation and dehydrogenation. Ni, Ru and Pt have been described as active phases in the hydrogenation reaction [9], at temperatures between 120 and 260 °C and pressures between 50 and 200 bar depending on the molecules.

In both cases, reduced metals are the most active phases, with Pt being the metal most widely proposed as the active phase for both reactions. However, as mentioned in the reactor design, important differences are found between both reactions. In the presence of high hydrogen pressures, reaction pathways of unsaturated organics are straightforward, with the consecutive hydrogenation of the different unsaturations of the molecules. In addition, carbon–heteroatom bond hydrogenolysis or ring-opening reactions (main undesired lateral reactions) require higher temperatures than the hydrogenation of carbon–carbon bonds, as it is possible to obtain higher hydrogenation selectivities by optimizing reaction conditions.

By contrast, dehydrogenation reactions are more complex, the operation at low hydrogen partial pressures, as well as the higher temperatures needed for the endothermic reaction, promote the presence of undesired reactions, as cracking of the organic compounds, which lead to a loss of efficiency of the LOHC-based systems. These lateral reactions can be also promoted by surface acid sites (even weak sites) of common cata-

lyst support, as the alumina-based ones. From the point of view of the metal dispersion, both hydrogenation and dehydrogenation reactions are promoted with the smallest metal crystallite sizes [10].

Another key aspect related to both catalytic processes and still understudied is catalyst stability. The viability of LOHC technology relies on being able to use these catalysts for many successive cycles. Both reactions can lead to catalyst deactivation by different mechanisms, especially coking and metal sintering. As a conclusion, although very promising, the development of LOHC-based technologies is still immature; aspects such as the stability of the LOHCs in successive hydrogenation/dehydrogenation cycles, the development of selective and stable catalysts or the design of optimized hydrogenation (to be built at the central hydrogen generation facility) and dehydrogenation (at the hydrogen utilization site) reactors must be improved for ensuring the viability of these approaches.

The use of carbon materials allows us to overcome several of the challenges reported previously. Among these materials, activated carbons are only promising supports for small molecular size LOHCs (for example in the toluene-methyl-cyclohexane). For larger aromatic or heterocyclic molecules, the microporous character of most of the activated carbons will lead to important intra-particle mass transfer effects. However, these effects can be overcome with other carbonaceous materials, such as carbon nanotubes, carbon nanofibers, high surface area graphites (HSAG) or graphenes. These materials are characterized by large surface areas (promoting the formation of small active phase crystallites), high chemical inertness of the surface, and open-pore structures that facilitate pore diffusion of reactants and products.

Other advantages of carbon materials are related to the ease of shaping, both at the macro- and micro-scale. As an example of the first approach, a carbon coating can be added with tailored properties (width, porous structure, surface chemistry) to monoliths, foams, and other intensified reactor components. Another positive consequence of these properties is the ease of manufacturing catalysts and catalytic structure of low density, being this fact of key interest in the design of large reactors. As an example of this fact, Oh and Kim [11] propose the use of carbon-coated alumina as catalysts when using nitrogenated LOHCs.

However, the key advantage of carbon supports is their low surface reactivity, especially if compared with the common inorganic supports, as alumina-based supports. This low reactivity minimizes the extent of the formation of cracking and oligomerization by-products, increasing the reaction selectivities and minimizing deactivation.

Several examples have been reported in the literature that demonstrate the advantages of carbon-based materials in hydrogenation reactions, even in the case of furanic compounds (with a largely more complex chemistry. For example, Faba et al. [12], report the use of high surface area graphites (HSAG) as supports that combine a mesoporous character (no mass transfer effects with these large molecules), chemical inertia (minimizing lateral reactions) and easiness for preparing supported metal catalysts. All these features lead to very active and selective hydrogenation/dehydrogenation catalysts. In the same way, different works summarized in the literature [2,3,9] and references cited therein mention the role of carbon supports in obtaining highly dispersed catalysts useful for these reactions.

In conclusion, carbon materials (especially non-microporous ones), open an interesting window for preparing the highly active and stable catalysts needed for chemical hydrogen storage using LOHCs. An increasing number of articles, patents and industrial developments are expected to appear in the forthcoming years.

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