New Perspectives in Hydrogen Storage Based on RCH2NH2/RCN Couples

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New Perspectives in Hydrogen Storage Based on RCH_2NH_2/RCN Couples.

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A recent breakthrough on primary amine dehydrogenation by an oxidant-free process, and without any hydrogen acceptor, opens the possibility for RCH_2NH_2/RCN couples to be considered as potential hydrogen energy carriers. Both hydrogenation and dehydrogenation processes can be catalysed by ruthenium complexes in rather mild conditions. This emerging exciting approach could be the starting point for the development of valuable economical systems.

Introduction

Finding an alternative energy vector to the actual fossil fuel economy is an attractive area of research, and during the last decade, the search for suitable hydrogen storage systems has received a large attention. In the context of the "Hydrogen Energy Economy" cycle, hydrogen storage remains a major challenge with a 2017 goal defined by the US Department of Energy (DOE) at 5.5 wt % with 40g.L^{-1} of hydrogen available for technical system targets.[1] Different approaches have been explored but they all suffer from various limitations. For example: a) in the case of compressed dihydrogen, problems due to a very high pressure technology and public acceptance, b) for liquid dihydrogen, the requirement of harsh cryogenic conditions, c) low bonding energies in porous materials imply pressures and temperatures far away from ambient conditions to achieve an efficient physisorption storage.

Chemical hydrogen storage represents an attractive route for future hydrogen carrier systems.[2] So far, most of the systems involve solid state materials such as hydrides (e.g. MgH_2),[3] complex hydrides,[4] or σ-H_2 gel materials.[5, 6] As opposed to physical storage, high bonding energies require high temperature cycles to promote hydrogen loss. Ammonia-borane is an appealing molecule that fulfil many requirements,[7, 8] but despite some recent advances,[9, 10] the absence of an efficient reversible process from the dehydrogenated sink products, borazine and polymeric B-N, remains a limitation. For all these reasons new emerging solutions have to be explored. Intuitively, liquid chemical hydrogen carriers have a few advantages, such as their compatibility with the existing fossil fuel infrastructures and liquid transport and storage facilities. Liquid transfer is easy to manage under ambient temperature without any pressure safety conditions. Thus, liquid organic hydrogen carriers can be considered as an alternative approach. Hydrogenated/ dehydrogenated heterocycles such as carbazole or boron-nitrogen compounds have been already studied,[11-19] but other sources have to be explored. Interesting systems rely on formic acid dehydrogenation at ruthenium,[20, 21] or iron,[22] and very recently, Beller *et al.* were able to demonstrate aqueous-phase methanol dehydrogenation and reforming at moderate temperature (72°C). The ruthenium-catalysed reaction in the presence of a base led to a H_2:CO_2 mixture in a 3:1 ratio.[23] In that context, and based on some recent breakthroughs, this frontier article focuses on the possibility to implement a primary amine/nitrile system as a liquid organic hydrogen carrier (LOHC) under catalytic conditions.

Discussion

In principle, there is a large scope of liquid substrates that could be involved in reversible hydrogen carriers. They can be prepared from fossil fuels but more advantageously from biomass. Primary amines/nitriles represent two well-known classes of compounds for chemists, and their synthesis is well-handled from several sources. From each CH_2NH_2 fragment present in a molecule, two equivalents of dihydrogen might be available which represents 13.3 wt % of hydrogen per CH_2NH_2 unit. The smallest available nitrile is acetonitrile but its associated primary amine, methyl amine, is a gas at ambient conditions (room temperature and atmospheric pressure). Thus, amine/nitrile couples with longer hydrocarbon chains have to be considered as potential liquid hydrogenated and dehydrogenated forms, even if the gravimetric percentage will be reduced. For example, butylamine and propionitrile or 1,5-diaminopentane and 1,3-pentanedinitrile are liquids in a large range of temperature and display suitable hydrogen contents. Further research will be needed to find the ideal liquid couple to fulfil the different requirements (see Conclusions).

Nitrile hydrogenation has been intensively investigated, hydrogenation of adiponitrile being one of the most important industrial process involved in the production of Nylon-6,6.[24] It is important to note that systems operating in mild conditions remain extremely limited. Some recent advances were reported by the groups of Morris[25] and Beller,[26] and in 2010 we disclosed that the dihydridebis(dihydrogen)bis(tricyclopentylphosphine) ruthenium complex $[RuH_2(H_2)_2(PCyp_3)_2]$ (**1**)[27] acted as a catalyst precursor in very mild conditions.[28] High activity and selectivity were achieved, at room temperature under 3 bar of dihydrogen, for the hydrogenation of the model substrate benzonitrile into benzylamine. The catalysis could even be performed without any solvent (Figure 1).

Reversible catalytic dehydrogenation is even more challenging. Until the very recent work from the Szymczak's group,[29] amine dehydrogenation required hydrogen acceptors or additives such as oxidant or base in stoichiometric or excess amounts.[30-32] It is noteworthy that the presence of any additive would prohibit applications using primary amines as hydrogen carriers. Szymczak's communication represents a significant breakthrough in the domain.[29] By using the pincer-type ruthenium complex $[HRu(bmpi)(PPh_3)_2]$ (**2**) they were able to dehydrogenate primary amines into the corresponding nitriles under relatively smooth conditions: preforming the reaction in refluxing toluene opened to a N_2 atmosphere avoided the use of a hydrogen acceptor (Figure 1). Their demonstration that dehydrogenation was inhibited by an increasing pressure of H_2 when operating in a closed vessel, opens the possibility to build a system on demand. Dehydrogenation is very selective and can be conducted with various aliphatic and benzylic primary amines. Furthermore, tolerance to a few functional groups has been exemplified. Such an easy dehydrogenation reaction represents an important step to fulfil the key-requirements for an efficient hydrogen storage system.

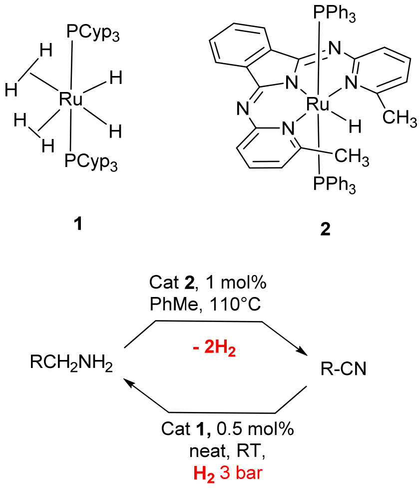

Figure 1: Complex **1** is a catalyst precursor for nitrile hydrogenation. Complex **2** is a catalyst precursor for amine dehydrogenation.

Based on these recent findings, one can envision some future research guidelines in order to build an efficient device. For example, accumulation of nitrile could inhibit the catalytic process by competition with primary amine coordination to the catalyst. This problem should stimulate research to design other catalysts able to prevent competitive coordination of nitrile, but keeping the advantages found with the ruthenium catalyst. Preliminary observations made by the authors suggest that the mechanism follows a pathway similar to that previously described for alcohol dehydrogenation.[33] Deeper investigations are needed in order to optimize the reaction conditions and the catalyst nature for primary amine/nitrile systems as liquid organic hydrogen carrier applications. The development of such a hydrogen carrier system is exciting due to the possibility to use a technology compatible with fossil fuel infrastructures and existing modes of transport for liquids. The vehicle technology has been developed over more than one century and is well mastered by all the on board vehicle industry. Liquid transfer could be easily managed under ambient temperature without pressure safety conditions. Moreover, heat management during transport and reaction of liquids should be easy. One main difference with the fossil fuel economy concerns the refilling step. An exchange will be needed instead of a simple refilling at the "fuel station" (or more appropriate named LOHC Station) in order to replace the dehydrogenated liquid by a fresh hydrogenated one. Dehydrogenated compounds could then be regenerated by a catalysed hydrogenation step under smooth conditions, *e.g* room temperature and low H_2 pressure, a process which has also to be optimized. Recyclable hydrogenation could be done either on small local plants at the fuel station which will modify the economy fuel distribution or, for larger scales, at industrial plants.[12]

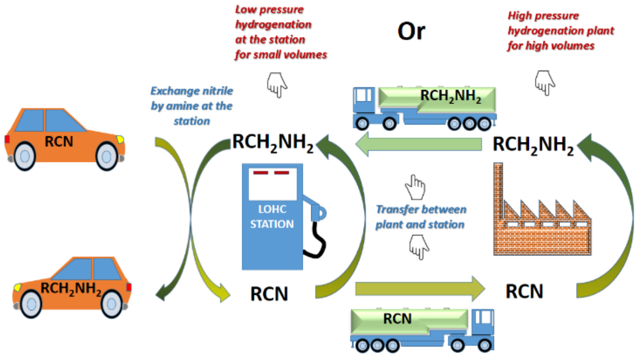

Figure 2: A possible LOHC facility from an amine/nitrile couple

Alternatively, liquid couples could be suitable systems for portable power equipments and for materials handling equipments.[34]

Conclusions

Recent advances have demonstrated the high potential of ruthenium complexes both for the hydrogenation of nitriles and the dehydrogenation of amines in mild conditions. It thus appears highly desirable to open a new research field based on the RCH_2NH_2/RCN couple as a hydrogen carrier. Key issues should be addressed in the future, and the following points summarize some of them together with some required specifications.

a) Choose the right RCH_2NH_2/RCN liquid couple with a high gravimetric hydrogen carrier potential.

b) Find an efficient catalyst precursor (transition metal complex or organic) ideally cheap, stable and operating at low loading. It might be advantageous to look for some supported catalysts in order in particular to improve the stability and/or the recovery of the catalyst precursors. The choice on homogeneous or heterogeneous catalysts will depend on the technical system targets (efficiency, stability, selectivity, diffusion problems…).

c) Perform the two reactions, hydrogenation/dehydrogenation, without any additives.

d) Keep the operating conditions close to room temperature both for dehydrogenation and hydrogenation while operating at low pressure of H_2 for hydrogenation.

e) Solvent-free reactions both for dehydrogenation and hydrogenation. Since a solvent-free reaction is needed to improve the gravimetric balance of the system, an alternative route might involve initial mixing of high gravimetric solids $R(CH_2NH_2)n/R(CN)n$ into liquid RCH_2NH_2/RCN couples while keeping the system in the liquid state all along the process. This mixture could lead to gravimetric % fitting the desired performances.

More research is needed before the development of sustainable long-term devices based on liquid organic hydrogen carriers, but focusing on RCH_2NH_2/RCN couples sounds like a very promising area.

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Biography

***Mary Grellier** received his PhD in 1996, from the University of Strasbourg, with Michel Pfeffer. He is "Maître de Conférences" at the University of Toulouse. His research at the LCC mainly concerns coordination and catalysis in organometallic chemistry.*

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Notes and references

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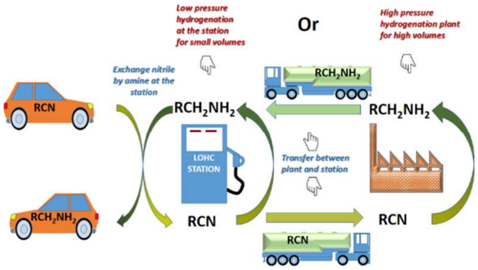

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