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Preface

Catalysis in hydrolysis of sodium borohydride and ammonia borane, and electrocatalysis in oxidation of sodium borohydride

We do not ignore that today we are living an unprecedented energy crisis, which is the diseased fruit of our intense use of depleting carbonaceous resources (*e.g.* coal, oil and gases) and of the subsequent greenhouse gas emissions (*i.e.* global warming and climate change). Since we have become aware of these facts and of their urgency, there has been an almost-unanimous consensus in devoting many (political, societal, environmental, financial, industrial, scientific and technological) efforts to move towards a sustainable world. Sustainability has become *the key word* of the 3rd millennium and, logically and expectably, it has become *one of the key words* in science, especially in energy and chemistry. Finding renewable, alternative energies while mitigating the greenhouse gas emissions is now our, scientists, ultimate challenge. And, catalysis undoubtedly plays *a key role* in this.

Hydrogen as energy source/carrier has in the recent decades emerged and is now often presented as being one of the most promising solutions to address the energy and environment issues aforementioned and to meet our future energy needs. Such an expectation is in fact not new. In the 19th century, the French famous novelist Jules Verne formulated this in his famous novel entitled *L'Ile Mystérieuse* (1874) through one of his fictitious hero: "I believe that water will one day be employed as a fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light [. . .]. Some day the coalrooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases, which will burn in the furnaces with enormous calorific power. There is, therefore, nothing to fear. As long as the earth is inhabited it will supply the wants of its inhabitants [. . .] I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future." What is impressive in these few sentences Jules Verne wrote is that some of the attributes of hydrogen (namely, *water* as a green, renewable, *inexhaustible* hydrogen source; its high energy density or its *enormous calorific power*) and almost all of the scientific/technological issues the hydrogen economy encounters nowadays (production from *water*; storage in *condensed* state; end use as energy source) are unambiguously reported.

Hydrogen storage is particularly problematic while it represents *a key* factor for many technological applications (vehicular, mobile and portable). Several approaches (*e.g.* pressurized hydrogen, cryogenic storage, porous materials, and chemical storage) are intensely investigated but none is mature enough for implementation yet. In this context, solid-state chemical hydrogen storage has notably attracted great attention in the past decade owing to *e.g.* the high hydrogen densities the studied materials have. This is particularly the case of boron-based hydrides. In the late 1990s, sodium borohydride ($NaBH_4$, sodium tetrahydridoborate, gravimetric hydrogen density of 10.8 wt%) was introduced as being a very promising material due to the fact that it can be used as hydrogen carrier (*i.e.* hydrogen source) and as energy carrier (*i.e.* direct fuel) for fuel cells. Then, in the middle of the 2000s, ammonia borane (NH_3BH_3, borazane, gravimetric hydrogen density of 19.5 wt%) was, in turn, presented as being a potential alternative to sodium borohydride to be used mainly as hydrogen carrier (it is noteworthy that using ammonia borane as direct fuel of fuel cells has been also regarded but the research has not been developed since then).

Sodium borohydride and ammonia borane stores hydrogen in hydride form and a facile route to dehydrogenate both compounds is hydrolysis:

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2 \quad (1)$$

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \quad (2)$$

Both reactions take place in room conditions, which makes them very attractive compared to other storage technologies. Nevertheless, in both cases, the reaction, *i.e.* the hydrogen release, has to be catalyzed and this can be done by an acid (liquid or solid) or a metal catalyst (heterogeneous or homogeneous). A rapid survey of the literature dedicated to each compound shows that most of the papers published so far have focused on developing reactive and durable metal-based catalysts. Sodium borohydride can also be considered as an energy (electrons) carrier and thus as a direct fuel of direct liquid-fed fuel cells. Sodium borohydride can be oxidized into sodium metaborate in alkaline conditions and this reaction liberates a high number of electrons:

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \quad E^0 = -1.24\,V_{ESH} \quad (3)$$

The challenge with this reaction is to avoid the occurrence of a side-reaction that is none other than the hydrolysis of sodium borohydride. In other words, the underlying challenge is to find a metal-based electrocatalyst that is active towards oxidation while being inert towards hydrolysis. Many works have been published in the past decades and research has clearly turned to noble metals like gold and silver. The objective is to get 8 electrons per sodium borohydride. To sum up, it is clear that catalysis plays *a key role* here.

Though many metal-based catalysts in various forms have been tested in both hydrolysis and oxidation so far, the fundamentals of the reactions and those related to the catalysts (*i.e.* role, nature

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of the active sites, stability of the surface, reasons of the catalysts deactivation, etc.) are still rather unknown. Furthermore, the reactions, especially the electrooxidation of sodium borohydride, are rather complex, involving short-living intermediates that are difficult to isolate, identify and characterize. To better control these reactions, we believe that the catalysis of these reactions has first to be better understood.

The idea of this Special Issue was born out of fruitful seminars and discussions in 2010 with several colleagues expert in catalysis, who pertinently remarked that many of the papers about these reactions are published in journals which *aims and scopes* are not primarily *catalysis*. This Special Issue is thus an opportunity to gives the (electro-) catalysis community an overview of the fundamental and technical problems that hinder the development of efficient, selective, durable catalysts. We hope that this Special Issue will open a wider discussion that might be helpful for all in better understanding the catalyst role and the reaction mechanisms, in improving the catalyst durability and selectivity, and in generating new ideas for the elaboration of supported catalysts with prospects of scale-up.

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