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## **LaNi<sub>5</sub> intermetallic both as catalyst and storage compound for in situ hydrogen generation from water under visible light irradiation**

### **Abstract :**

The intermetallic compound LaNi<sub>5</sub> has been shown both to catalyze, under visible light irradiation, the in situ photogeneration of hydrogen from water in a model system using Ru(bpy)<sub>3</sub><sup>2+</sup> as a photosensitizer, and to partially store the hydrogen so produced in the form of a hydride LaNi<sub>5</sub>H<sub>x</sub>. The stored hydrogen can be easily released by moderate heating of the hydride. This leads to the regeneration of the catalyst that can be used again for another cycle of catalysis – partial storage – hydrogen desorption.

### **Introduction**

The numerous episodes of weather extremes related to climate change have drawn awareness of the need to replace fossil fuels (petroleum, coal...) by developing renewable and non-polluting sources of energy, in particular solar energy. Although the latter source of energy is abundant, free and inexhaustible, it has the disadvantage of being intermittent and irregular. Consequently, there is a need to convert it into a form of energy that can be stored and transported rendering it readily available. Photochemical conversion allows the transformation of water into the energy carrier hydrogen by visible light irradiation [1-5]. Hydrogen is a clean energy source as its air combustion leads to pure water. Apart from production, storage is also a problem and most often hydrogen is stored as a gas under pressure. Another storage approach with hydrogen trapped in a solid has been developed using intermetallic compounds such as LaNi<sub>5</sub> that are able to rapidly absorb and desorb large amounts of H<sub>2</sub> through the formation of the LaNi<sub>5</sub>H<sub>6</sub> hydride, under mild conditions of temperature and pressure [6-10].

In 1978 we developed one of the first efficient systems for the photoreduction of water to hydrogen by visible light irradiation using Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) as photosensitizer and colloidal Pt as catalyst [2,11]. This system, which is of no commercial interest, has been extensively used as a model to evaluate catalysts and we developed a systematic study of heterogeneous catalysts based on this model [12,13]. Using this approach we have shown that colloidal metals, substrates or powders, and metal oxides act as catalysts. Amongst the metals, we have examined non noble metals, and particularly nickel [2,12] which is more abundant and less expensive than platinum. Moreover, in this model system nickel nanoparticle catalysts have shown good efficiency, but the production of hydrogen stopped rapidly [12]. The efficiency is increased when bimetallic Ni-Pd (10% Pd) particles are used [14]. In search of other nickel-based

catalysts more stable under the reaction conditions, we undertook the study of intermetallic compounds such as  $\text{LaNi}_5$ . These compounds have been widely studied in recent years due to their capacity to rapidly absorb large amounts of hydrogen to form the  $\text{LaNi}_5\text{H}_6$  hydride and then release this hydrogen under mild temperature and pressure [15-17]. In this study,  $\text{LaNi}_5$  powder is shown both to catalyze the in situ photochemical production of hydrogen from water and to partially store the hydrogen so produced.

## Experimental

The procedures and apparatus for continuous irradiations (between 400 nm and 600 nm) and for  $\text{H}_2$  production measurements have been describe elsewhere [2,12]. The sources of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ , methyl viologen  $\text{MV}^{2+}$ , EDTA and colloidal Pt have been specified previously [2,12]. We used samples of  $\text{LaNi}_5$  given by Annick Percheron-Guégan [18].

## Results and Discussion

To test the catalytic efficiency of  $\text{LaNi}_5$  in the reduction of water to hydrogen, we chose the well-known system  $\text{Ru}(\text{bpy})_3^{2+}$ / methyl viologen  $\text{MV}^{2+}$ /ethylene diamine tetra-acetic acid EDTA/colloidal Pt/ $\text{H}_2\text{O}$  [12,19] while replacing the Pt catalyst with  $\text{LaNi}_5$  powder. The reference system has been fully characterized and optimized [12, 20] as regards the quantum yield of hydrogen formation. In this study, we used the optimized concentrations [12, 20] of  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{MV}^{2+}$ , and EDTA, namely  $5.65 \times 10^{-5}\text{M}$ ,  $3 \times 10^{-3}\text{M}$ , and  $0.1\text{M}$ , respectively, and varied the  $\text{LaNi}_5$  concentration at pH5.

Upon irradiation of an aqueous solution containing these four compounds with visible light ( $\lambda > 400 \text{ nm}$ ), we observe the formation of hydrogen that is easily identified by gas phase chromatography as previously described [12]. The quantity of hydrogen formed depends on the  $\text{LaNi}_5$  concentration. We have estimated the quantum yield of hydrogen formation  $\phi'(1/2 \text{ H}_2)$  for 2mg of  $\text{LaNi}_5$  to be 0.036. This quantum yield is the lower limit of the true efficiency as it does not take into account the diffusion of light by the  $\text{LaNi}_5$  particles. This  $\phi'(1/2 \text{ H}_2)$  value is lower than that of colloidal nickel, 0.06 [12]. However, contrary to the case of colloidal nickel where hydrogen formation stops after an hour, in the presence of  $\text{LaNi}_5$  the reaction continues for more than 20 hours. It would appear that the addition of a rare earth metal such as lanthanum increases the stability of nickel without affecting its catalytic properties. The lifetime of the system can be measured by the number of cycles (turnover number TN) conducted by the various elements of the system. Figure 1 represents the turnovers relative to  $\text{LaNi}_5$ ,  $\text{TN}(\text{LaNi}_5)$ , as a function of the quantity of  $\text{LaNi}_5$  in solution.

Figure 1 shows that the turnover is greater than 1 and attains 92.1 for 0.5 mg of  $\text{LaNi}_5$ . The values of  $\text{TN}(\text{LaNi}_5)$  measured as a function of the quantity of  $\text{LaNi}_5$  in solution and the corresponding curve in Figure 1 whose shape is characteristic, show unambiguously that  $\text{LaNi}_5$  catalyzes the reduction of water to  $\text{H}_2$ . It should be noted that  $\text{LaNi}_5$  has been shown to be as effective as conventional catalysts in the hydrogenation of carbon monoxide CO and in the hydrogenolysis of hydrocarbons [18].

The fact that the reaction stops after 20 hours might indicate, as is the case of Pt or of Ni, the existence of secondary reactions, particularly the hydrogenation of  $\text{MV}^{2+}$  [12,19]. We have previously shown that this secondary reaction can be inhibited by catalyst poisons such as glutathione GSH [12,19]. When we add GSH to the  $\text{Ru}(\text{bpy})_3^{2+}$ / methyl viologen  $\text{MV}^{2+}$ /ethylene

diamine tetra-acetic acid EDTA/ LaNi<sub>5</sub> powder system we don't observe an increase in the turnover relative to either LaNi<sub>5</sub> or MV<sup>2+</sup>. On the contrary to Ni or Pt, LaNi<sub>5</sub> doesn't seem to catalyze the hydrogenation reaction of MV<sup>2+</sup>.

An explanation of why the reaction stops could be the absorption of hydrogen by LaNi<sub>5</sub> to form the hydride LaNi<sub>5</sub>H<sub>6</sub>. It should be noted that it has been demonstrated that suspensions of LaNi<sub>5</sub>H<sub>x</sub> in n-undecane [21] or water [22] absorb H<sub>2</sub>. To test this hypothesis, we recovered the LaNi<sub>5</sub> catalyst by filtering at the end of the experiment. The catalyst was placed under argon atmosphere and upon heating in a water bath at 85°C we detected hydrogen by gas phase chromatography. In a second set of experiments, we placed a trap consisting of a tube filled with LaNi<sub>5</sub> powder between the irradiation cell and the burette used to measure gas volume. The irradiation cell contained an aqueous solution of Ru(bpy)<sub>3</sub><sup>2+</sup>/MV<sup>2+</sup>/EDTA/Catalyst with either LaNi<sub>5</sub> powder or colloidal Pt as the catalyst. The volume of H<sub>2</sub> measured in the presence of the trap is lower than the volume of H<sub>2</sub> measured in the absence of the trap. At the end of the experiment, we also checked that the LaNi<sub>5</sub> in the trap that had been swept through by the photochemically-produced hydrogen contained hydrogen. As previously, we heated the trap of LaNi<sub>5</sub> in a water bath and used gas phase chromatography to measure the resulting H<sub>2</sub>. Consequently, the number of cycles measured and reported in Figure 1 is underestimated. It is important to note that the LaNi<sub>5</sub> powder used as a catalyst is again able to catalyze the reduction of water upon removal of the absorbed hydrogen by heating. The same sample of LaNi<sub>5</sub> can thus be used for several cycles of catalysis / storage / H<sub>2</sub> desorption.

This study shows that LaNi<sub>5</sub> powder is a catalyst for the in situ photoproduction of hydrogen from water, which suggest that Ni nanoparticles are formed under visible irradiation [12, 23]. It also shows that LaNi<sub>5</sub> in powder form is capable to partially absorb the hydrogen produced photochemically probably to yield the LaNi<sub>5</sub>H<sub>x</sub> hydride [6, 24]. The catalyst can be recycled by mild heating to release the absorbed hydrogen.

In conclusion, whatever the mechanism, this study establishes a new approach to the catalytic photoproduction of hydrogen and its applications. An intermetallic compound such as LaNi<sub>5</sub> has the advantage of facilitating the storage and separation of hydrogen from other gases eventually produced leading to very pure hydrogen. This intermetallic compound also facilitates the transportation of H<sub>2</sub> in the form of solid hydride. Such a study can be extended to related LaNi<sub>5</sub>-based alloys and other intermetallic compounds [6, 7, 25] to test their catalytic activity in reactions of practical interest. In the simultaneous production of H<sub>2</sub> and O<sub>2</sub> from water under visible light irradiation, LaNi<sub>5</sub> is a promising candidate as it avoids the recombination reaction of these two gases [3].

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### Figure caption

Catalytic turnover numbers  $TN(\text{LaNi}_5)$  for  $\text{H}_2$  generation by the visible-light irradiation of aqueous solutions (pH5) containing  $\text{Ru}(\text{bpy})_3^{2+}$   $5.65 \times 10^{-5}\text{M}$ ,  $\text{MV}^{2+}$   $3 \times 10^{-3}\text{M}$ , EDTA  $0.1\text{M}$  and various amounts of  $\text{LaNi}_5$  powder. The turnover numbers  $TN(\text{LaNi}_5)$  are defined as the ratio of the total  $\text{H}_2$  amount to the initial amount of  $\text{LaNi}_5$ .

