

In-situ generated nanocatalysts for NaBH₄ hydrolysis studied by liquid phase calorimetry: influence of the nature of the metal on the H₂ production rate

Anthony Garron¹, Simona Bennici¹, Aline Auroux^{1*}

¹ Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS/Université Lyon1, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex (France)

*aline.auroux@ircelyon.univ-lyon1.fr

Introduction

Hydrogen and fuel cell technologies are currently in an intense development phase. Among the most suitable and safe technologies for hydrogen storage, metal borohydrides have a potential for portable and stationary applications due to their high energy density storage at room temperature and atmospheric pressure. Hydrogen can be released through the hydrolysis reaction $\text{BH}_4^- + 4\text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + 4\text{H}_2$, which can be controlled catalytically. Moreover this reaction produces pure and slightly humid hydrogen directly usable in a PEM fuel cell. The only by-product is sodium metaborate, which is soluble in water and environmentally benign. However an appropriate catalyst is necessary to carry out the reaction at a high rate.

Catalytic materials less costly than Pt or Ru have been studied for this purpose [1,2]. Since the major limiting step for the reaction is known to be the accessibility of the active sites, the use of nanoparticles is of great interest [3,4]. A series of metal salts were tested according to a protocol which involves the in-situ generation of nanoparticles [5]. Microcalorimetric techniques were used to determine the heats of the hydrolysis reaction and to explain the differences in the kinetic behaviors observed with the various metals.

Materials and Methods

Metal nanoparticles were generated by addition of Fe(III), Co(II), Ni(II) chloride salts to an aqueous solution of NaBH₄. The suspension of catalyst generated in-situ was then brought to pH 14 by addition of soda and tested in a "semi-batch" regime by subsequent additions of NaBH₄ solution stabilized by soda. Two concentrations of sodium borohydride were used, 2 and 19 wt% respectively. The reaction was performed at 30°C and atmospheric pressure under stirring in a differential reaction calorimeter. Additionally to the measurement of the calorimetric signal, the volume of hydrogen released was measured as a function of time after drying in a liquid nitrogen trap, using a volumetric gas-meter.

Results and Discussion

Fig. 1 presents the volumes of hydrogen evolved at 1, 3, 8, 15, 25, 55 and 120 min respectively upon the first addition of a high concentration solution of NaBH₄ to the Co and Ni catalysts generated in-situ (10 mL of a 19 wt% NaBH₄ solution stabilized by 10 mmol NaOH (4 wt%)). Evidently, the Co based catalyst is twice as active as nickel, itself 10 times more active than iron (not shown). Complementary characterization studies (TEM, magnetism, XRD ...) of the in-situ metal catalysts before and after test confirmed the formation of Co and Ni borides,

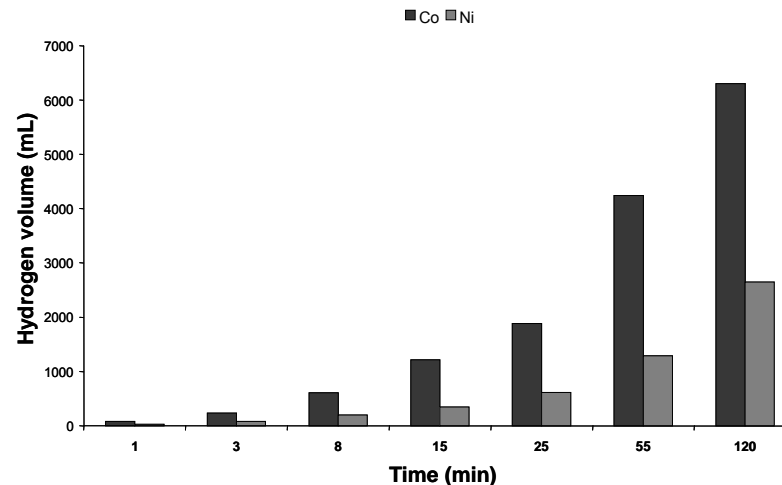
which are the real active phase, while iron remained mostly in a metallic form. Both Ni and Co catalysts displayed similar activities in low and high concentration borohydride solutions.

The heats of reaction were measured and found to be around $-245 \text{ kJ} \cdot \text{mol}^{-1} \text{NaBH}_4$ for the first five injections. The calorimetric technique made it possible to assess the stability of the catalysts by recording the variations of the temperature differential.

Significance

It has been demonstrated that metals which can be readily oxidized and form stable boride species are the best catalysts for the borohydride hydrolysis reaction, at a lower cost compared to precious metals. Their performances are similar using low or high concentration NaBH₄ solutions, and the rate of hydrogen generation remains constant during the reaction.

Figure 1. Hydrogen volume generated at 1, 3, 8, 15, 25, 55 and 120 minutes from the hydrolysis of high concentration solution (19 wt% NaBH₄) in presence of nanocatalysts.



References

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