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

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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 BH₄⁻ + 4H₂O → B(OH)₄⁻ + 4H₂, 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%)). 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.