

An innovative calorimetric investigation of the kinetics of hydrogen release from catalyzed hydrolysis of borohydrides

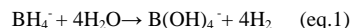
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Introduction

During the last decade a lot of research effort has been put into the development of suitable and safe technologies for hydrogen storage. Sodium and potassium borohydrides (NaBH₄ and KBH₄) are two interesting materials for future energy applications and in particular for hydrogen storage [1]. They present the advantages of a high potential hydrogen density together with a safe and easy hydrogen release through a hydrolysis reaction (eq. 1) that can be controlled catalytically.



In spite of the abundance of kinetic data in the literature, the thermodynamic features of the catalyzed hydrolysis are not yet well understood. Calorimetric techniques, and liquid phase calorimetry in particular, are promising methods to study catalytic reactions [2]. In this work we show that the total enthalpy of the hydrolysis reaction depends on the catalytic system used and that the reaction of hydrolysis of borohydrides is a complex one, featuring different phenomena.

Materials and Methods

A Setaram Titrys microcalorimeter was used to determine the enthalpies of hydrolysis in a system where water, solutions of cobalt nanoparticles, or solutions of organic acids were added in excess to pure solid NaBH₄ and KBH₄. The instrument used was a Calvet differential heat flow microcalorimeter modified to allow continuous stirring of liquid samples. Pre-heated solutions (303 K) were added to both sample and reference cells simultaneously using a programmable syringe pump. The measurement cell was linked to a volumetric gas-meter in order to determine the amount of hydrogen evolved and the kinetics of the reaction.

Results and Discussion

The experimental calorimetric curves obtained with NaBH₄ are presented in Fig. 1. In the conditions where a large excess of water was added to anhydrous sodium borohydride at 303 K, it took two days to complete the hydrolysis of NaBH₄, while the reaction time was only 45 min when using solutions of cobalt nanoparticles, and 30 min for malic acid. Taking into account the energy of +32 kJ·mol⁻¹ NaBH₄ consumed to dissociate NaBH₄ into Na⁺ and BH₄⁻ [3] and the loss of water vapor at 303 K with an estimated energy of 7.4 kJ·mol⁻¹ NaBH₄ [4], the calorimetric measurement of a total energy of -212.6 kJ·mol⁻¹ NaBH₄ corresponds to an

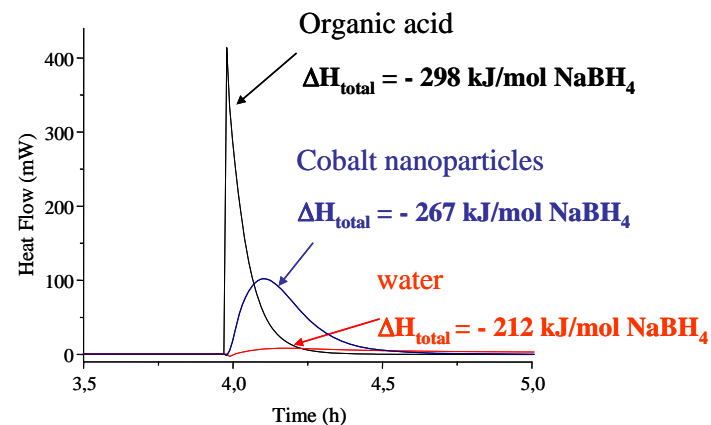
experimentally determined reaction energy of about -252 kJ·mol⁻¹ NaBH₄, a value in good agreement with the theoretical value of -250.5 kJ·mol⁻¹ NaBH₄. When using Co nanoparticles, the total energy increased up to -267 kJ·mol⁻¹ NaBH₄, due to the energy released during activation of the catalyst. Finally, a value of -298 kJ·mol⁻¹ NaBH₄ was measured upon injection of a malic acid solution. The drastic increase in the total energy of reaction can be attributed to secondary reactions involving the organic molecules.

The total energy values for the hydrolysis of KBH₄ have also been studied under the same conditions, providing a complete thermodynamic picture of the hydrolysis reaction.

Significance

The measurement of the heat evolved upon hydrogen generation by hydrolysis of borohydrides is essential for assessing the thermal risks related with the performance of a reacting system where a rapid increase in the temperature may result in a sharp pressure increase. Moreover, the thermodynamic data associated to the kinetics of hydrogen release allowed us to determine the reaction mechanism.

Figure 1. Heat flow signals (Titrys calorimeter) versus time for the additions of 1 mL of pure water, 1 mL malic acid solution, or 1 mL cobalt nanoparticles in suspension, on 30 mg solid NaBH₄.



References

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