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Kinetic modeling of self-hydrolysis of aqueous NaBH₄ solutions by model-based isoconversional method

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ARTICLE INFO

Article history:

Received 10 October 2013

Received in revised form

4 February 2014

Accepted 6 February 2014

Available online 1 March 2014

Keywords:

Sodium borohydride

Self-hydrolysis

Kinetics

Isoconversional method

Hydrogen production

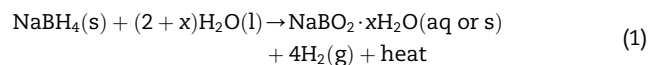
ABSTRACT

The present work reports the kinetic modeling of self-hydrolysis of non-buffered, non-stabilized NaBH₄ solutions by model-based isoconversional method. The overall kinetics is described by a ‘reaction-order’ model in a practical operating window of 10–20 wt% NaBH₄ solutions at 25–80 °C and 0–50% conversions. The apparent activation energy and pre-exponential factor are interrelated through a kinetic compensation effect (KCE). The apparent reaction order remains constant at a given temperature irrespective of extent of conversion and decreases with increase in temperature. It decreases from first-order to 0.26 with increase in temperature from 25 to 80 °C. The apparent activation energy is found to increase from 65 ± 11 to 162 ± 2 kJ mol⁻¹ with increase in extent of conversion from 0 to 50%. The variation of parameters with extent of conversion is discussed based on changes in solution properties during the progress of hydrolysis reaction.

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Introduction

Sodium borohydride (NaBH₄) undergoes self-hydrolysis in the presence of water while generating hydrogen according to [1–3]:



where x is the excess hydration factor [2].

The overall conversion of this reaction at room temperature is 7–8% [4,5], making it inappropriate for a practical H₂

generator. Certain metal catalysts accelerate the reactant conversion and metal-catalyzed hydrolysis is being accepted as a potential technology for delivering H₂ to portable fuel cells [6–9]. While the conversion of NaBH₄ is accelerated by metal-catalyzed hydrolysis, self-hydrolysis still occurs to some extent at low temperatures and becomes significant at elevated temperatures. This needs to be arrested for increasing the shelf-life of the reactant solution [10–14].

There are also unresolved issues such as the minimization of the amount of water and the nature of hydration of metaborate by-products which limit the net or usable hydrogen storage capacities [2]. An alternative method, steam

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<http://dx.doi.org/10.1016/j.ijhydene.2014.02.035>