



Mechanism and kinetics of sodium borohydride hydrolysis over crystalline nickel and nickel boride and amorphous nickel–boron nanoparticles

Zhijie Wu^{a, c, *}, Xikang Mao^a, Qin Zi^a, Rongrong Zhang^a, Tao Dou^a, Alex C.K. Yip^{b, **}

^a State Key Laboratory of Heavy Oil Processing and the Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing 102249, China

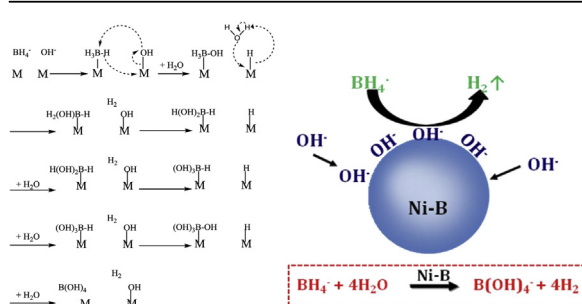
^b Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

^c Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China

HIGHLIGHTS

- A reaction route to describe borohydride hydrolysis over nickel catalysts.
- Presence of boron in nickel catalyst change hydrolysis routes.
- Nickel catalysts containing boron possess good hydrolysis activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 February 2014

Received in revised form

11 June 2014

Accepted 12 June 2014

Available online 20 June 2014

Keywords:

Borohydride

Hydrolysis

Hydrogen

Nickel catalyst

Amorphous nickel–boron nanoparticles

ABSTRACT

The initial hydrogen generation turnover rates during the hydrolysis of sodium borohydride over nickel catalysts (crystalline nickel (Ni), crystalline nickel boride (Ni₃B), and amorphous nickel–boron (Ni–B) nanoparticles) were measured to investigate the reaction kinetics and mechanisms by varying the reactant concentrations and reaction temperatures. Nickel catalysts with and without boron follow different hydrolysis pathways; hydroxide ions are involved in the activation of reactant molecules over Ni₃B and Ni–B catalysts. This study explicitly reports the zero-order and first-order reaction kinetics with respect to the reactant concentration over Ni, Ni₃B and Ni–B catalysts. The initial hydrogen generation turnover rates and activation energies determined from the experimental data indicate that the amorphous Ni–B nanoparticles exhibit the highest turnover rate and lowest activation energy for the hydrolysis of borohydride among the investigated catalysts. This study provides a general strategy for the development of borohydride hydrolysis catalysts via the modification of a metal catalyst using boron, which causes the crystalline structure to become amorphous and leads to electron-rich, highly under-coordinated metal atoms at the surface.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding author. State Key Laboratory of Heavy Oil Processing and the Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing 102249, China. Tel.: +86 10 8973 3235; fax: +86 10 8973 4979.

** Corresponding author.

E-mail addresses: zhijiewu@cup.edu.cn, zhijie.wu@hotmail.com (Z. Wu), alex.yip@canterbury.ac.nz (A.C.K. Yip).

1. Introduction

Hydride salts such as sodium borohydride (NaBH₄) can be used as safe hydrogen reservoirs for the polymer electrolyte membrane fuel cells [1,2]. In general, metal, bimetallic or metal–boron catalysts

are used to hydrolyse sodium borohydride and then generate hydrogen in a controlled manner [2–6]. To design and synthesise hydrolysis catalysts that possess high activity under high borohydride concentrations and low temperatures, the reaction mechanisms/pathways must be understood. Extensive studies of borohydride hydrolysis pathways and kinetics have been performed using novel metal and metal-boron catalysts [5–9]. Nevertheless, the effect of the reactant concentration on the hydrogen generation rate is difficult to ascertain based on the kinetics of the proposed pathways [3,10–19] because of a lack of information regarding the kinetically relevant steps [5–9,10].

The hydrolysis of sodium borohydride over Ru catalysts is generally hypothesised to be a first-order reaction with respect to the reactant concentration, whereas this hydrolysis catalysed by transition metals (Ni, Co, Fe) has been reported to be a zero-order reaction [1,5–19]. These first- and zero-order dependences can be explained by the Langmuir–Hinshelwood model for the single-site adsorption of BH_4^- onto the catalyst [1,14]. However, these previous kinetic studies did not consider the effect of the hydroxide ion concentrations on the reaction rates. For example, amorphous nickel–boron (Ni–B) and cobalt–boron (Co–B) catalysts exhibit high hydrogen generation rates in alkaline borohydride solutions with high hydroxide ion concentrations or low borohydride concentrations, whereas Ru catalysts exhibit high hydrogen generation rates under the opposite conditions [5–18]. These results indicate that hydroxide ions play a crucial role in the hydrolysis of borohydride on catalyst surfaces. In our previous work, we proposed that hydroxide ions substitute the hydrogen in BH_4^- to form $\text{BH}_{4-y}(\text{OH})_y$ ($y = 1, 2, 3, 4$) [18]. To further validate this proposed mechanism, the kinetic relevance of the elementary steps and the effects of the metal species (crystalline nickel (Ni), crystalline nickel boride (Ni_3B), or amorphous nickel–boron (Ni–B)) on the initial hydrogen generation turnover rates during the hydrolysis of borohydride were examined by varying the reactant concentrations.

Herein, we report the intrinsic hydrolysis activities (denoted as the initial hydrogen generation turnover rates) of crystalline Ni and Ni_3B and of amorphous Ni–B clusters in the hydrolysis of sodium borohydride. We aim to provide a mechanistic interpretation of the kinetic data and to contrast the behaviour of a Ni metal surface with that of a Ni metal surface containing B atoms. Although the hydrolysis of borohydride over transition metals (Ni, Fe and Co) has been reported to be a zero-order reaction with respect to the borohydride concentrations [8,17], our recent studies [18] and some other reports [10–17] have shown that, when amorphous Ni/Co/Fe–boron nanoparticle catalysts are employed, the hydrolysis of borohydride is a first-order reaction with respect to the borohydride concentration and proceeds via different reaction intermediates on the surfaces of the metal–boron catalyst. We hypothesize that the different intermediates formed over different active sites (i.e., Ni, Ni_3B and Ni–B) under the same reaction conditions can explain this interesting kinetic behaviour. Based on the work of Peña-Alonso et al. [1], Guella et al. [5,6] and Holbrook et al. [8], we propose herein a modified hydrogen generation mechanism that involves hydroxide ions for the hydrolysis of borohydride over Ni–B catalysts, as illustrated in Fig. 1. First, borohydride and hydroxide ions in the solution are chemisorbed to the metal atoms. A proton on the borohydride ion then exchanges with a hydroxide ion to form M–H , which can further react with water to generate hydrogen gas. We attribute the different kinetic behaviours of metal and metal–boron nanoparticles during borohydride hydrolysis to the differences in the reaction pathways that occur at their surfaces. These behaviours on metal–boron catalysts are consistent irrespective of the boron contents and particle sizes.

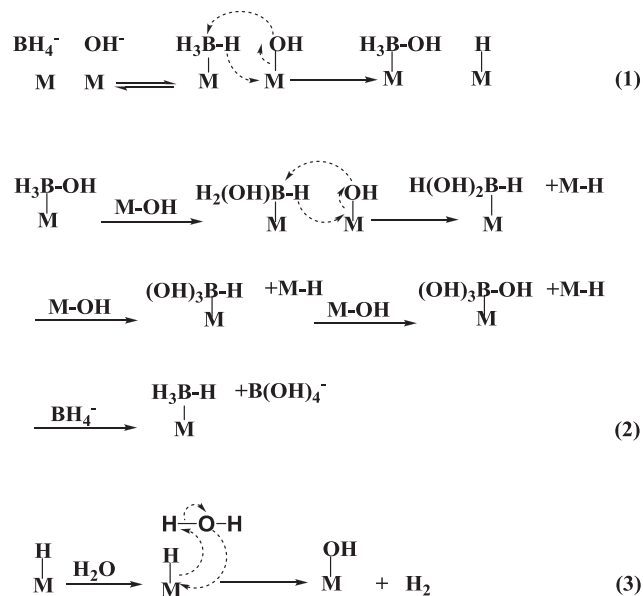


Fig. 1. The proposed mechanism for catalytic hydrogen production via hydrolysis from an aqueous borohydride solution.

2. Experimental

2.1. Materials

NaBH_4 (98%) and ethylenediamine (99.9%) were purchased from J&K Scientific, Ltd. (China). Nickel chloride (99.99%), nickel sulphate (99.99%), ethanol (99.99%), tetraethylene glycol (99%), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80 wt. %) and KBH_4 (98%) were purchased from Guanfu Chemical, Ltd. (Tianjin, China) and were used as received. The catalyst synthesis procedures described in Refs. [19–22] were used to prepare the Ni, Ni_3B , Ni–B-1 and Ni–B-2 catalysts, respectively.

Ni catalyst [19]: 2.1 g of nickel chloride was dissolved in 30.0 mL of ethanol, and then 10.0 g of an 80 wt.% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution and 10.0 mL of a 25 mol L^{-1} NaOH aqueous solution were added under stirring (800 rpm). The reaction was continued for several hours under stirring until bubbles were no longer released at room temperature. The obtained black nano-nickel catalyst was washed with distilled water until reaching a pH of 7, then washed five times with ethanol to remove the water and finally stored in ethanol.

Ni_3B catalyst [20]: 0.12 g of nickel chloride was dissolved in 15.0 mL of tetraethylene glycol (TEG) under ultrasonication for 10 min, and then the mixture was stirred (800 rpm) at 318 K under an Ar purge for 60 min. Subsequently, 15 mL of a previously freshly prepared and chilled solution of TEG and 0.50 g of KBH_4 were added dropwise (0.05 mL s^{-1}) to the metal salt solution. With continuous stirring under an Ar purge, the temperature was slowly ramped to 553 K and held for 5 min. Then, the reaction solution was cooled to room temperature, and the precipitates were collected by centrifugation, washed five times with ethanol, and dried under vacuum at 313 K for 12 h.

Ni–B-1 with a Ni/B molar ratio of 2 [21]: 11.1 mL of ethylenediamine was dissolved in 1800.0 mL of deionised water, and then 11.8 g of nickel chloride and 9.0 g of KBH_4 were added to the aqueous ethylenediamine solution under stirring (800 rpm), respectively. The pH of the solution was adjusted to 12.5–13.0 through the addition of 0.1 mol L^{-1} NaOH. To prepare amorphous Ni–B-1 nanoparticles, the solution was heated to 313 K. The reaction was continued until no bubbles were observed, and the resulting black solid was washed with distilled water until pH = 7,

Download English Version:

<https://daneshyari.com/en/article/7736230>

Download Persian Version:

<https://daneshyari.com/article/7736230>

[Daneshyari.com](https://daneshyari.com)