Various Rate Law Orders Through Hydrolysis of Sodium Borohydride Over Co-M-Zr-B (M= Cr, Mo and W) Nano Catalyst

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ABSTRACT

This article describes a Group (VI) modified Co-Zr-B amorphous nano alloys were prepared in situ ultrasound-assisted reduction by sodium borohydride in an aqueous solution. Co-Cr-Zr-B, Co-Mo-Zr-B and Co-W-Zr-B powders were characterized by XRD, FESEM, BET and ICP techniques. No distinct peak could be observed in XRD patterns of the obtained catalysts indicating that all samples possessed amorphous structure. Indeed, it was not seen any metal oxide phase. Obtained powders are highly active catalysts for hydrogen generation from the hydrolysis of sodium borohydride. The reported work also includes the full experimental details for the collection of a wealth of kinetic data to determine the activation energy and effects of the catalyst dosage, amount of NaBH4, and temperature on the rate of the catalytic hydrolysis of sodium borohydride. Rate law orders of all catalysts were calculated from an Arrhenius plot of each catalyst.

KEYWORDS

Amorphous Materials, Hydrogen Generation, Kinetics, Nanostructures, Rate Law
1. INTRODUCTION

At the present time, there is a significant interest in the study and use of metal nanoclusters because of their novel and attractive physical and chemical properties (Schmid, 1992). For example, transition metal nanoclusters have been studied as catalysts in various organic and inorganic reactions (Weddle, Aiken, & Finke, 1998). Recently, sodium borohydride has been suggested as a new fuel source for supplying hydrogen under mild conditions (Amendola, Sharp-Goldman, Janjua, Spencer et al., 2000). NaBH₄ yields hydrogen gas and water-soluble sodium metaborate, NaBO₂, upon hydrolysis in the presence of certain catalysts (Equation (1)):

\[ \text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 \]  

The first hydrogen generation from borohydride hydrolysis was taken in 1950s (Schlesinger, Brown, Hoekstra, & Rapp, 1953). The reaction product (borax) is environmentally clean and can be recycled to the reactant NaBH₄ (Kojima & Haga, 2003). It is found that, NaBH₄ solution hydrolyzed only when certain suitable catalysts are added. Many precious metal materials, such as Ru supported on Pt (Bai, Wu, Wu, & Yi, 2006) and Pd (Guella, Zanchetta, Patton, & Miotello, 2006) supported on carbon, Pt-Ru supported on metal oxide (Krishnan, Yang, Lee, & Kim, 2005), have been used as catalysts for this reaction. However, such kind of catalysts seems to be not suitable for the industrial application considering their cost and availability. There are many reports about non-noble metal catalysts for the hydrolysis of NaBH₄, such as Co-B (Zhang, Hou, Zhang, Wang, & Li, 2012), Ni-B (Li, Li, Dai, & Qiao, 2003) and three elemental catalysts of Co-Ni-B (Fernandes, Patel, Miotello, & Filippi, 2009; Ingersoll, Mani, Thenmozhiyil, & Muthalaih, 2007; Li, Wu, Zhang, Dai, & Qiao, 2004). Co-B was paid considerable attention for its good catalytic activity, low cost and simple preparation method. There have been many papers reporting the preparation and catalytic properties of Co-B catalysts (Amendola, Sharp-Goldman, Janjua, Kelly, et al., 2000; Gardiner & Collat, 1965; Holbrook & Twist, 1971; Jeong et al., 2007; Jeong et al., 2005; Kaufman & Sen, 1985; Lee et al., 2007; Liu, Li, & Suda, 2006; Tong, Luo, & Chu, 2008; Walter, Zurawski, Montgomery, Thornburg, & Revankar, 2008; Wu, Wu, Bai, Yi, & Zhang, 2005; Zhao, Ma, & Chen, 2007). They were usually synthesized by mixing a Cobalt salt solution with a sodium borohydride solution. Amorphous Co-B catalysts, prepared by reduction of metal salts with a reducing agent, have attracted great attention in catalysis owing to their unique properties such as isotropic structure, high concentration of coordinative unsaturated sites, relevant chemical stability, and low cost (Pei et al., 2007). However, the exothermic nature of the reduction reaction involves high surface energy causing metal–boride particles to agglomerate. This particle agglomeration lowers the effective surface area of the catalyst powder thus limiting its catalytic activity. Ultrasonication has proven a useful technique for inducing chemical reaction and inhibiting particle agglomeration due to the chemical effects from acoustic cavitation, which produces unusual chemical environments (Mulvany, Cooper, Griers, & Meisel, 1990; Suslick, Choe, Cichowlas, & Grinstaff, 1991). Ultrasonic assisted synthesis of metal-boride powders improves the catalytic activity of the metal-boride catalysts. Indeed, reduction reaction of metals solution by ultrasonication method increases of specific surface areas of obtained powders. Previously, we have synthesized Co-La-Zr-B quaternary amorphous nano alloy for hydrogen generation through hydrolysis of sodium borohydride (Loghmani & Shojaei, 2013b). Next attempt was done by investigation of PVP and triphenylphosphine role on size, morphology and catalytic activity of crystalized Co-La-Zr-B nano powder (Loghmani & Shojaei, 2013a, 2015). We have also tried to investigate role of oleic acid as stabilizing agent on size and morphology of quaternary nano catalyst (Loghmani & Shojaei, 2014) and several polymers and surfactants on size, morphology and catalytic activity of ternary Cu–Fe–B nanocatalysts (Loghmani, Shojaei, & Khakzad, 2017). Yuan and co-workers (Yuan, Chen, Lu, & Chen, 2008) have synthesized amorphous Co-Zr-B, having a
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