STUDY ON THE HYDROGEN STORAGE PROPERTIES OF $Ca(BH_4)_2$ COMPOSITES USING TAGUCHI METHOD

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Abstract

The hydrogen storage properties of $Ca(BH_4)_2$ composites for hydrogen energy applications was studied since light metal borohydrides $Ca(BH_4)_2$ have great potential as an effective hydrogen storage facility. This study has been conducted to improve $Ca(BH_4)_2$'s hydrogen storage efficiency, such as doping with different types of catalysts. In this study, in order to improve the selection of the better hydrogen storage properties, Taguchi Method is being selected as a suitable statistical approach to analyse the optimum factors and responses. The objective of this study is to analyse the performance characteristic of hydrogen storage by employing the signal-to-noise ratio and the analysis of variance (AnoVa). In this analysis, material and catalyst are the two factors that are being considered. To analyse the relative importance of the method parameter, analysis of variance (AnoVa) was performed. First, the material and system both are insignificant on decomposition temperature. Next, on hydrogen release both material and catalyst are significant. Finally, on activation energy, both material and catalyst are insignificant. The required material and catalyst that have been chosen to obtain an optimum temperature are on decomposition temperature are ($Ca(BH_4)_2$)_MgH and None, while on hydrogen release are Ca(BH4)2 and none, and lastly on activation energy are $Ca(BH_4)_2$ and NbF_5. The signal-to-noise ratio can analyse that the optimum parameter on decomposition temperature is at 250°C, on the hydrogen release is 9.6wt%, and on the activation energy is 51kJ/mol. In other words, Taguchi optimization can be a good method to enhance potential selective material preparation and catalyst to improve hydrogen storage properties in the future.

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1. Background of Study

Hydrogen has attracted a great deal of attention among researchers as an ideal energy carrier used as a medium for transporting and storing energy. Due to high gravimetric capability and favourable safety consideration, hydrogen storage in a solid-state shape has been one of the alternative methods compared to compressed gas and liquid hydrogen storage. Various materials have been suggested and are currently being studied [1].As alternative hydrogen storage materials, complex hydrides, such as metal alanates and borohydrides, are attractive candidates due to their high gravimetric and volumetric hydrogen densities [2-6]. Light metal borohydrides ($Ca(BH_4)_2$) have great potential as an effective hydrogen storage facility. The relative high theoretical hydrogen storage potential of $Ca(BH_4)_2$ is around 11.6 wt%[7]. However, $Ca(BH_4)_2$ has drawbacks in terms of high desorption temperature, sluggish desorption kinetics and weak reversibility conditions, making it difficult to use them in a hydrogen storage device[8]. A number of studies have been conducted to improve Ca(BH4)2's hydrogen storage efficiency, such as doping with different types of catalysts, such as $TiCl_3$[9], NbF_5[10] and TiF_3[11]. In this analysis, in order to boost the hydrogen storage properties through a mutual interaction between the two hydrides, the hydrogen storage properties of the $Ca(BH_4)_2$ with various catalysts were also investigated.

1.1 Literature

Previous studies and methods have been performed with the addition of catalyst to boost the composite of alanate-borohydride ($Ca(BH_4)_2$). Furthermore, metal hydride-based catalysts have been found to be one of the best catalysts for enhancing the storage properties of solid-state hydrogen storage materials. The report by Huang et.al further indicates that, with the addition of $TiCl_3$ and Pd as catalysts, the mixture of CaB_6 and CaH_2, the reaction dehydrogenation ingredients, is only partly hydrogenated to $Ca(BH_4)_2$ even at a high temperature of 400-440 °C for 48 h under a high H_2 pressure of 700 bar[12]. Besides, in order to enhancing the hydrogen storage properties, reactive hydride composite (RHC) concept introduced. One of the alternative approaches focused on various hydride mutual interactions was found to be the RHC concept, which changes both the kinetics and thermodynamics of the hydrogen sorption reaction [11, 13-18].

N.S Mustafa et.al stated that in their previous study[1], it is possible to observed the lower onset desorption temperature for the $2NaAlH_4$ + $Ca(BH_4)_2$ composite system as compared with milled $NaAlH_4$ and $Ca(BH_4)_2$.The relative destabilization of $2NaAlH_4$ and $Ca(BH_4)_2$ in the $2NaAlH_4$+ $Ca(BH_4)_2$ reactive hydride composite contributes to the creation of new compounds after dehydrogenation, including Al-Ca, Al-B, and Ca-B alloys. For more rapid sorption kinetics and lower decomposition temperature of the composite system, these alloys are expected to play an important role. While this composite has enhanced its hydrogen storage properties, the efficiency of kinetics is still slow and the temperature of decomposition for functional use is very high.

Vajo et al. [12] suggested the concept of destabilization in a $2LiBH_4$+MgH_2 system. When $LiBH_4$ and MgH_2 are mixed, MgB_2 is formed instead of B during the dehydrogenation process, resulting in decreased reaction enthalpy and increased reversibility. The destabilization of reactants is also found to be efficient to $Ca(BH_4)_2$ [19, 20], and other systems [21-23]. By modifying the reaction pathway, the combined $Ca(BH_4)_2$+MgH_2 system shows enhanced reversibility relative to pure $Ca(BH_4)_2$ [19]. In the second dehydrogenation cycle, a power retention of 60 percent, equivalent to ca 5.0 wt. percent H_2, is achieved after heating to 400 °C for the post-dehydrogenated $Ca(BH_4)_2$+MgH_2 method at 400 °C for 2 h and then re-hydrogenated at 350 °C and 90 bar H2 for 24 h, while $Ca(BH_4)_2$ is not reversible under the same setting[19].

1.2 Problem Statement

Hydrogen storage properties do influence performance of metal hydrides. On this composite, a metathesis reaction occurred after mechanochemical treatment of a mixture of NaAlH4 single bond ($Ca(BH_4)_2$) leading to partial formation of NaBH4 and $Ca(AlH_4)_2$ [24]. No research on the catalytic effect of ($Ca(BH_4)_2$) on improving the hydrogen storage efficiency of $NaBH_4$ has been conducted up to this date. ($Ca(BH_4)_2$) synthesized by hydrothermal methods shows major changes in the hydrogenation efficiency of MgH_2 from our previous studies[25]. Therefore, it is assumed that this unique ($Ca(BH_4)_2$) would also provide impressive improvements in the hydrogen storage efficiency of metal borohydride

($NaBH_4$). And so it is important to research the addition of ($Ca(BH_4)_2$) as the catalyst and its catalytic effect on the efficiency of $NaBH_4$. In this study, efficiency changes and potential catalytic pathways will be investigated and substantiated by the results of the experiments[26]. The Taguchi Method is used to analyze the optimum condition of the control factors which are materials and catalysts, knowing either the materials and catalysts are suitable for obtaining the optimum condition of the responses which is decomposition temperature, hydrogen release and activation energy. In this study, material and catalyst elements are used as control factors that affect the value of decomposition temperature, % of hydrogen release and the value of activation energy. Analysis of the factors and values of hydrogen properties is carried out using data from previous studies to obtain optimal features using the Taguchi Method. The best control factor varies with the highest single-to-noise (S/N) ratios where the data are used to evaluate the optimal condition of a control factor(materials and catalyst) while Analysis of Variance (AnoVa) data are used to analyze a relevant control factor[27].

1.3 Objective

To perform:

1. Analysis of Variance (AnoVa) of Signal to Noise (S/N) ratio for onset decomposition temperature, Hydrogen release and activation energy [Nur Naqibah Baddrun]
2. "Smaller the better" S/N ratio and optimum condition analysis for onset decomposition temperature [Nur Aliyah Syafiqah Ahamad]
3. "Larger the better" S/N ratio and optimum condition analysis for Hydrogen release [Aiman Mashkur Masnu Amira]
4. "Smaller the better" S/N ratio and optimum condition analysis for activation energy [Sharifah Hanan Abdullah]