



Effect of FeCl₃ Addition On The Dehydrogenation Properties Of 2NaAlH₄+Ca(BH₄)₂ Composite System For Solid State Hydrogen Storage

Nurul Shafikah Mohd Mustafa^{1,*}, Noor Azniza Mohd Noor¹, Zarina Omar¹, Muhammad Syarifuddin Yahya¹, Mohammad Ismail¹

¹ Energy Storage Research Group, Faculty of Ocean Engineering Technology, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

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ABSTRACT

The imperative for renewable energy transition hinges on the development of efficient storage solutions, with hydrogen storage being a frontrunner due to its high energy yield and clean combustion profile. This study explores the enhancement of hydrogen storage properties via Iron (III) chloride (FeCl₃) doping into a 2NaAlH₄ + Ca(BH₄)₂ composite. Through a six-hour ball milling process, the transformation of NaAlH₄ and Ca(BH₄)₂ into Ca(AlH₄)₂ and NaBH₄ phases is achieved, setting a benchmark for subsequent analyses. We have delineated four principal dehydrogenation stages where FeCl₃ doping has substantially lowered the decomposition temperatures, as indicated by the onset of hydrogen release at 100 °C in the doped composite—a reduction from the 125 °C observed in the undoped material. These findings are substantiated by Differential Scanning Calorimetry (DSC) which confirms the lower temperature thresholds across all dehydrogenation stages, while Scanning Electron Microscopy (SEM) illustrates a uniform distribution of smaller, finer particles in the doped composite, suggesting an increased surface area that potentially enhances kinetic rates due to shorter diffusion paths for hydrogen. The insights from this research not only illuminate the effectiveness of FeCl₃ as a dopant in improving hydrogen storage capabilities but also highlight the broader implications of such materials in enhancing the practicality and efficiency of hydrogen as a renewable energy vector, thereby contributing to the collective efforts in overcoming the challenges of hydrogen storage.

1. Introduction

Hydrogen, a colorless and odorless gas at ambient conditions, encounters obstacles as a potential alternative fuel source, primarily due to concerns related to safety and storage. The conventional methods for storing hydrogen, including compression as gas or liquification, face challenges because hydrogen's low density necessitates large storage volumes, limiting its practicality. Solid-state hydrogen storage emerges as a promising solution to overcome these challenges, suitable for both stationary and mobile uses. An ideal material for solid-state storage would possess a high capacity

* Corresponding author.

E-mail address: nurulshafikah@umt.edu.my

for hydrogen storage by weight, release hydrogen at low temperatures, and support quick hydrogen absorption and desorption cycles, all at an economically viable cost. Employing solid-state storage techniques could make hydrogen a more viable and sustainable energy option, potentially decreasing dependence on conventional fossil fuels [1]. Research in materials science has led to significant advancements in solid-state hydrogen storage materials, such as metal hydrides and complex metal hydrides, renowned for their excellent storage capacities and quick hydrogen cycling. Efforts to refine these materials focus on optimizing their thermal and kinetic properties. Sodium aluminium hydride (NaAlH_4) and calcium borohydride ($\text{Ca}(\text{BH}_4)_2$) are highlighted for their exceptional gravimetric hydrogen storage potential [2,3]. NaAlH_4 , for instance, can store up to 5.5 wt.% hydrogen in two dehydrogenation steps, while $\text{Ca}(\text{BH}_4)_2$ has a theoretical capacity of 11.6 wt.%, although its actual capacity is lower due to kinetic barriers [3,4]. Despite their capacities, challenges persist, including the need for high operational temperatures and pressures and the impact of kinetic and stability barriers on effective hydrogen storage.

Several strategies have been adopted to tackle this challenge, including the use of catalysts, improving surface area and reaction rates through ball milling, and merging with other metals or complex hydrides to create a destabilization system [5-18]. This system has garnered significant interest from researchers, evidenced by the numerous studies dedicated to exploring its potential and effectiveness in enhancing hydrogen storage. In our prior study, we discovered that the composite system combining 2NaAlH_4 with $\text{Ca}(\text{BH}_4)_2$ outperformed the individual performances of milled NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$ in dehydrogenation efficiency [7]. The composite's dehydrogenation onset temperature was remarkably lowered to 125 °C, a substantial improvement compared to the unary components of NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$. This superior performance is attributed to the mutual destabilization between NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$, leading to the formation of novel alloys like Al–Ca, Al–B, and Ca–B after dehydrogenation. These alloys are key in enhancing sorption kinetics and reducing the decomposition temperature of the composite. Nevertheless, despite the improvements in hydrogen storage properties, the kinetics and decomposition temperature still need optimization for practical applications.

Expanding upon our earlier research, the integration of 5 wt.% TiF_3 as a catalyst into the 2NaAlH_4 - $\text{Ca}(\text{BH}_4)_2$ composite notably advanced its hydrogen release characteristics [19]. This strategic enhancement significantly lowered the initial dehydrogenation temperature for the composite's first decomposition stage from 125 °C to an impressive 60 °C. Additionally, this catalytic intervention decreased the activation energy for decomposition from the initial measurements of 142.9 kJ/mol and 146.5 kJ/mol to 79.3 kJ/mol and 124.6 kJ/mol, respectively, in the TiF_3 -doped composite. Building on our previous research, we have noted a gap in the exploration of catalyst addition to reactive hydride composites (RHC), particularly the $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ system, beyond our own investigations. Our selection of FeCl_3 as a catalyst is based on its potential to refine dehydrogenation pathways and reduce activation energies, thereby enhancing hydrogen storage performance. Consequently, we are examining the effects of a 10 wt% FeCl_3 catalyst on the $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ composite to advance hydrogen storage technology. This choice is supported by FeCl_3 's demonstrated ability to facilitate the dehydrogenation of complex hydrides and destabilized solid-state hydrogen storage systems. For example, Zhang and colleagues [20] highlighted FeCl_3 's significant impact on the destabilized LiNH_2 – 2LiH system, noting that a mere 1 mol% of FeCl_3 decreased the decomposition activation energy by 14.93 kJ/mol relative to the uncatalyzed system. Similarly, Chu *et al.*, [16] reported that FeCl_3 could lower the decomposition temperature of $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ from 283 °C to 232 °C, while also reducing the activation energy from 129.7 kJ/mol to 117.7 kJ/mol. Therefore, it is reasonable to deduce that FeCl_3 may exhibit considerable promise as

an additive to improve the dehydrogenation performances of the $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ composite system.

Hence, it is in the interest of this current work to explore the hydrogen storage properties and surface morphology characteristics of the $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ destabilized system with the effects of a 10 wt% FeCl_3 catalyst. Characterizations are presented on the basis of Sievert's pressure-composition-temperature (PCT), differential calorimetric scanning (DSC) and surface electron microscopy (SEM).

2. Methodology

Sodium alanate (NaAlH_4) of hydrogen storage grade, 93% pure, along with calcium borohydride ($\text{Ca}(\text{BH}_4)_2$) in powder form, and iron(III) chloride (FeCl_3) were procured from Sigma Aldrich. These initial substances were utilized directly without any additional purification. Handling of materials and the preparation of samples were conducted within an MBraun Unilab glove box. This glove box was maintained with a high-purity argon atmosphere to protect the samples from moisture and oxygen exposure. A blend of the non-doped and doped composites, with a 10 wt% concentration of FeCl_3 , underwent ball milling in a planetary ball mill (NQM-0.4). This process was carried out at a ball-to-powder weight ratio of 80:1, operating at 400 rpm for a duration of 6 hours.

A Sieverts-type pressure–composition–temperature (PCT) apparatus, provided by Advanced Materials Corporation, was employed to measure the initial desorption temperature and the kinetics of hydrogen release in the samples. The temperature of the samples increased from 25 °C to 550 °C at a rate of 5 °C per minute. The kinetics of isothermal dehydrogenation of the samples were analyzed at 420 °C, under hydrogen pressures of 1 atm.

X-ray diffraction (XRD) data were processed using a Rigaku MiniFlex X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation, operating at a rate of 2.00°/min across diffraction angles from 20° to 80°. Differential scanning calorimetry (DSC) measurements were conducted using a Mettler Toledo TGA/DSC 1 system. The samples were heated from ambient temperature to a predetermined temperature under a 50 mL/min flow of argon. The structural morphology of the samples was examined with a scanning electron microscope (SEM), specifically a JEOL JSM-6360LA model.

3. Results

3.1 Dehydrogenation properties

Figure 1 portrays the Temperature Programmed Desorption (TPD) curves that capture the dehydrogenation behavior of NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$ -based composites, both in their undoped form and when doped with 10 wt.% FeCl_3 . These curves are the crux of understanding how the thermal stability and hydrogen release characteristics of these materials are influenced by the doping process.

In the context of our prior research [7], we have observed a transformative effect post-milling, where the original composite constituents, NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$, undergo a structural evolution to $\text{Ca}(\text{AlH}_4)_2$ and NaBH_4 after a milling period of six hours. The significance of this structural evolution becomes evident during the dehydrogenation process, which, as illustrated, encompasses four major reactions. The initial phase of the reaction series involves the decomposition of $\text{Ca}(\text{AlH}_4)_2$ into CaAlH_5 , which occurs at the lower temperature range. In the undoped composite, this sequence initiates at 125 °C, progressing to a second phase at 178 °C, indicative of distinct thermal thresholds for the respective reaction stages.

The incorporation of FeCl_3 as a doping agent shifts these thermal thresholds downward, as seen in the modified TPD curves. The doped composite begins its hydrogen release at 100 °C for the first

stage and 150 °C for the second, signalling temperature reductions of 25 °C and 28 °C, respectively. This shift not only quantifies the catalytic effect of FeCl₃ doping but also qualitatively highlights its role in enhancing the composite's thermal responsiveness.

Moreover, the third and fourth reactions, corresponding to the breakdown of CaH₂ and NaBH₄, also reflect an improved release profile in the doped composite. Although the enhancement is modest, it nevertheless indicates a comprehensive impact of FeCl₃ across all stages of dehydrogenation.

The broader implications of these results cannot be overstated. The lower initiation temperatures for hydrogen release are indicative of a material that requires less energy input for hydrogen desorption, a pivotal attribute for practical hydrogen storage applications. By reducing the temperature requirements for dehydrogenation and enhancing the overall hydrogen release, this approach presents a viable pathway to more efficient hydrogen storage. These findings serve as a testament to the potential of targeted doping strategies in the advancement of material sciences, particularly in energy storage and conversion.

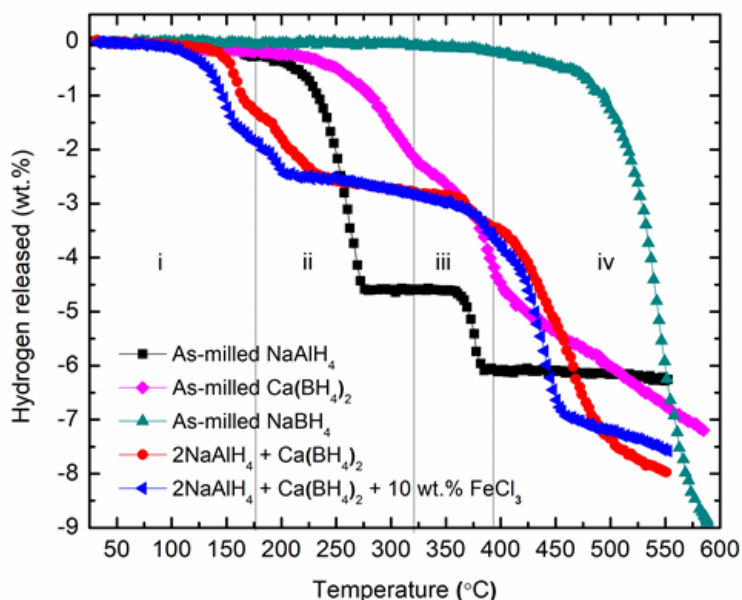


Fig. 1. TPD curves of the 2NaAlH₄ + Ca(BH₄)₂ and 2NaAlH₄ + Ca(BH₄)₂ + 10wt.% FeCl₃ composites

Figure 2 illustrates the isothermal dehydrogenation kinetics of both undoped and FeCl₃-doped composites at a consistent temperature of 420 °C, following their dehydrogenation processes. The kinetics observed in the FeCl₃-doped composite were substantially faster than those in its undoped counterpart, indicating a marked improvement in dehydrogenation efficiency with the addition of FeCl₃. Specifically, the composite doped with 10 wt.% FeCl₃ demonstrated a remarkable ability to release about 4.1 wt.% hydrogen within the initial 10 minutes of dehydrogenation—a significant increase compared to the mere 1.6 wt.% hydrogen released by the undoped composite in the same timeframe. Over a period of 60 minutes, the FeCl₃-doped composite continued to outperform, achieving a total hydrogen release of up to 4.9 wt.%, whereas the undoped composite only reached a hydrogen release of 3.0 wt.%.

These results highlight the profound impact of FeCl₃ doping on the dehydrogenation kinetics of the composite, significantly accelerating the rate of hydrogen release and achieving higher total hydrogen release over the observed period. The data clearly demonstrate that FeCl₃ not only

catalyzes a faster initial release of hydrogen but also contributes to a sustained higher rate of release, suggesting an improved efficiency and potential for hydrogen storage applications. This enhancement in dehydrogenation kinetics underscores the value of FeCl_3 as a doping agent, offering a promising approach to optimize the performance of hydrogen storage materials.

Therefore, the strategic incorporation of FeCl_3 into the composite material significantly bolsters its dehydrogenation kinetics, as evidenced by the faster and more extensive hydrogen release when compared to the undoped variant. This enhancement positions FeCl_3 -doped composites as superior candidates for efficient hydrogen storage solutions, emphasizing the importance of doping strategies in the development of advanced energy materials.

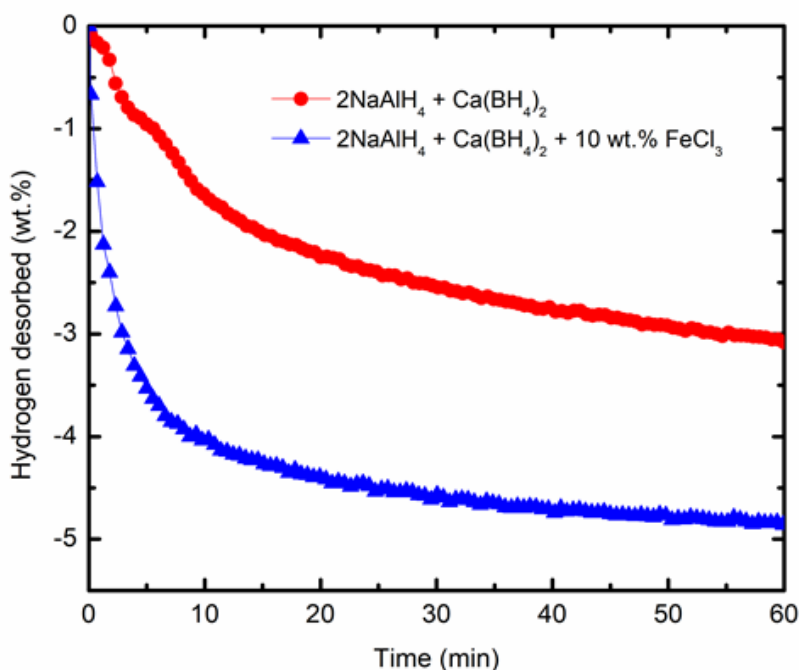


Fig. 2. Isothermal dehydrogenation kinetics of $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ and $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2 + 10\text{wt.}\% \text{FeCl}_3$ at 420°C under 1 atm

3.2 Differential Scanning Calorimetry (DSC)

In Figure 3, the Differential Scanning Calorimetry (DSC) profiles of both doped and undoped composites are examined as they are heated at a uniform rate of $30^\circ\text{C}/\text{min}$. The DSC curve of the undoped composite displays four major thermal events: an exothermic reaction at 190°C and three endothermic peaks at approximately 248°C , 358°C , and 470°C . These thermal signatures correlate with the stepwise decomposition of the composite, beginning with the conversion of $\text{Ca}(\text{AlH}_4)_2$ to CaAlH_5 , indicated by the first two peaks, and followed by the breakdown of CaH_2 and NaBH_4 for the last two peaks, respectively. Conversely, the DSC profile of the composite with 10 wt.% FeCl_3 doping reveals a notable shift with only three endothermic peaks, suggesting that the incorporation of FeCl_3 catalyzes a change in the decomposition behavior, leading to lower reaction onset temperatures for each stage of the process. The addition of FeCl_3 considerably lowers the energy barrier for the decomposition reactions, most significantly affecting the stability of the $\text{Ca}(\text{AlH}_4)_2$ and NaBH_4 phases.

The modified DSC pattern in the presence of FeCl_3 highlights not just a quantitative change in temperature but also a qualitative change in the thermal decomposition process of the composite. The reduction in decomposition temperatures implies that FeCl_3 acts as a catalyst, facilitating the release of hydrogen at reduced thermal inputs. This has profound implications for the practical

application of such composites in hydrogen storage, where lower activation temperatures can translate to energy savings and improved operational efficiencies.

Overall, the distinct differences in the DSC curves between the undoped and FeCl₃-doped composites underscore the substantial influence of doping on thermal behavior. The FeCl₃ doped material exhibits a clear shift to lower temperatures, underscoring the dopant's role in enhancing the composite's dehydrogenation characteristics. This finding contributes to a better understanding of how transition metal chlorides like FeCl₃ can modify the thermal properties of hydrogen storage materials, which is critical for their development and optimization for real-world energy applications.

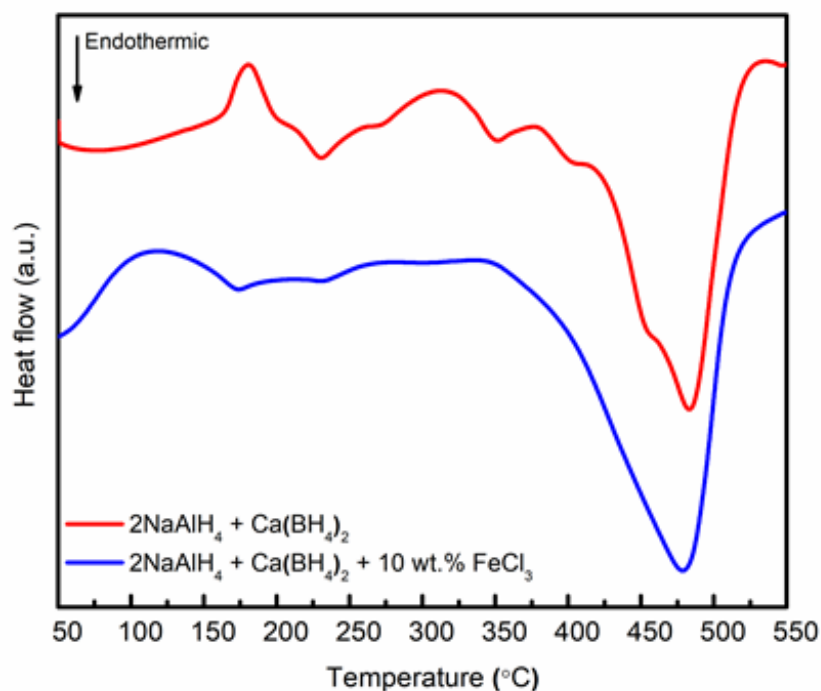


Fig. 3. DSC traces of the 2NaAlH₄ + Ca(BH₄)₂ and 2NaAlH₄ + Ca(BH₄)₂ + 10wt.% FeCl₃ composites at a heating rate of 30 °C/min

3.3 Scanning Electron Microscopy (SEM)

The SEM images presented in Figure 4(a) and (b) afford a detailed comparison between the morphologies of undoped and FeCl₃-doped composites. It is evident that the doped composite manifests a more uniform particle distribution, with particles that are noticeably smaller and finer in comparison to those of the undoped composite. This observation suggests that the doping process has likely contributed to a refinement in particle size, which is a significant factor when considering the kinetics of hydrogen sorption. A decrease in particle size corresponds to an increase in specific surface area, providing more active sites for interaction and potentially enhancing the kinetics of hydrogen sorption due to the shortened diffusion path length for hydrogen atoms.

Expanding on this, the enhanced kinetic rates afforded by smaller particle sizes are well-documented in existing literature [9,11,21]. The increased surface-to-volume ratio resulting from the finer particle sizes in the FeCl₃-doped composite means that hydrogen molecules have less distance to travel before being absorbed or desorbed, which could lead to a more efficient uptake and release of hydrogen. Additionally, this increase in surface area may facilitate a more effective distribution of the FeCl₃ catalyst throughout the composite, ensuring that the catalytic effect is maximized and thus further improving the hydrogen sorption kinetics.

Furthermore, the uniformity in particle distribution is likely to contribute to a more homogenous thermal behavior during dehydrogenation, as well as a consistent reaction environment. This uniformity ensures that all particles are more likely to experience similar conditions, which can lead to a more predictable and stable sorption performance.

In summary, the SEM analysis of the FeCl_3 -doped composite indicates significant microstructural differences from the undoped composite, particularly in particle size and distribution. These differences are critical as they likely play a direct role in the observed enhancement of the composite's sorption kinetics, emphasizing the importance of microstructural optimization in the development of high-performance hydrogen storage materials.

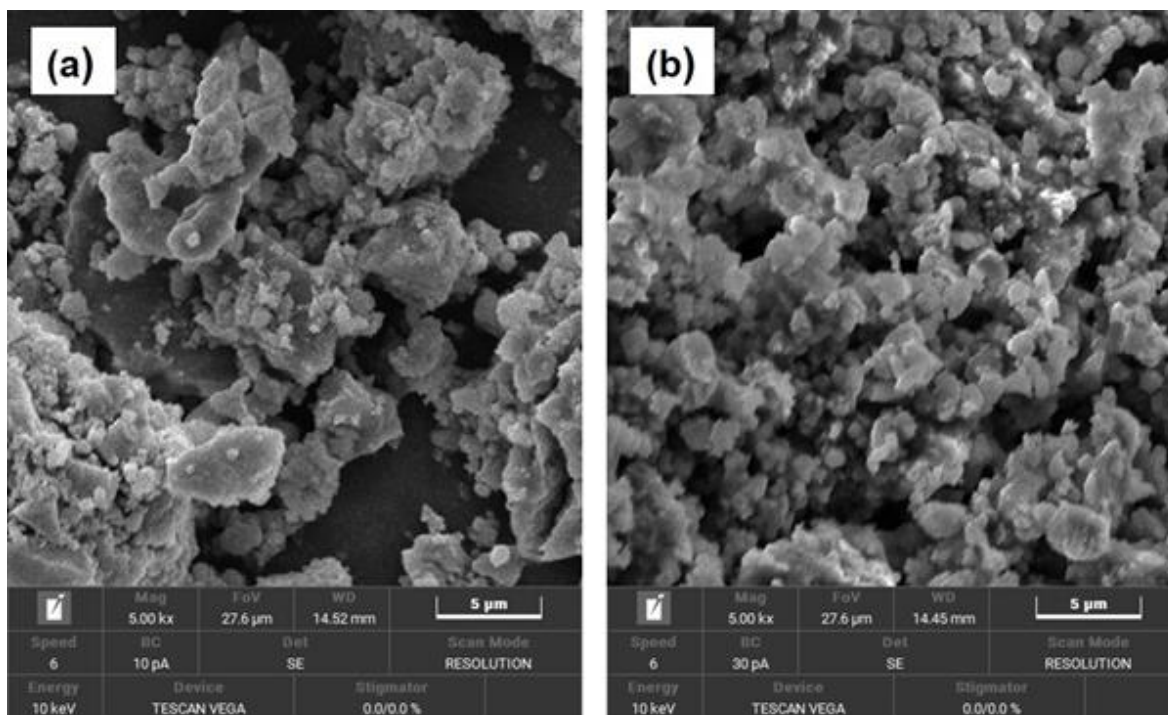


Fig. 4. SEM images of the (a) $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2$ composite and the (b) $2\text{NaAlH}_4 + \text{Ca}(\text{BH}_4)_2 + \text{FeCl}_3$ composite

4. Conclusions

In this study, the incorporation of Iron (III) chloride (FeCl_3) into NaAlH_4 and $\text{Ca}(\text{BH}_4)_2$ -based composites significantly enhances their hydrogen storage performance. DSC and SEM analyses, alongside TPD findings, provide a comprehensive view of the improvements achieved through FeCl_3 doping. The DSC results show a clear shift in decomposition temperatures to lower values, indicating that the presence of FeCl_3 facilitates the hydrogen release process at significantly reduced temperatures. Specifically, the onset of hydrogen release in the FeCl_3 -doped composite begins at $100\text{ }^\circ\text{C}$, a notable decrease that underscores the dopant's effectiveness in enhancing thermal responsiveness. SEM images further reveal that the doped composites possess a more uniform particle distribution, with smaller and finer particles compared to the undoped variant. This alteration in microstructure, leading to an increased specific surface area, likely contributes to the observed acceleration in hydrogen sorption kinetics due to shorter diffusion paths for hydrogen molecules. Combining these insights, our research illustrates that FeCl_3 doping not only lowers the energy barrier for hydrogen release, making the process more efficient, but also optimizes the material's microstructure for improved hydrogen storage capacity. The marked decrease in

decomposition temperature, coupled with enhanced sorption kinetics, positions FeCl₃-doped composites as a superior option for hydrogen storage applications. Thus, the study concludes that the strategic modification of composite materials through FeCl₃ doping presents a viable pathway toward the development of efficient, sustainable hydrogen storage solutions, promising significant advancements in energy storage and conversion technologies.

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