



Enhanced hydrogen storage properties of magnesium hydride using a KH-TiO₂-Nb₂O₅/carbon-coated nickel nanoparticles catalyst

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ABSTRACT

Magnesium hydride (MgH₂) is a promising hydrogen-storage material, but its slow sorption kinetics and high thermodynamic stability continue to limit practical implementation. In this work, we demonstrate an original and scalable approach to enhance MgH₂ performance by employing a catalyst prepared entirely from commercially available powders (KH, TiO₂, and Nb₂O₅), combined with commercial carbon-coated Ni nanoparticles (C@Ni). Unlike MXene-based catalysts widely reported in the literature, our catalyst system avoids complex and hazardous synthesis steps and enables industrially scalable processing. Two incorporation routes (one-step ball milling and a two-step mixing strategy) were evaluated. The catalyst decreased the dehydrogenation onset temperature from 321 °C to below 236 °C and reduced the activation energy from 152 to 93.8 kJ·mol⁻¹. The optimized material exhibited fast hydrogen desorption (6.38 wt% in 10 min at 300 °C) and a low-temperature absorption (5.77 wt% at 150 °C and 3.47 wt% at 75 °C), a performance not previously reported for catalyst systems derived solely from commercial precursors. Moderate cycling stability was also achieved, retaining approximately 79% capacity after 20 cycles. These results highlight the originality and practical relevance of a catalyst design strategy that enables high-performance MgH₂-based hydrogen storage without the need for laboratory-specific or non-scalable synthesis routes.

1. Introduction

Hydrogen (H₂) has the potential to replace conventional fossil fuels and power an environmentally sustainable civilization. However, under standard temperature and pressure, hydrogen has a low density, which presents significant storage challenges [1–3]. Because hydrogen has a low boiling point of 20.4 K at 1 atmosphere, it is stored in high-pressure tanks or cryogenic systems [2,4,5]. Therefore, this entails higher energy costs and safety hazards associated with storage and transportation [6, 7]. To solve the drawbacks of employing H₂ in its innate form, researchers have focused on solid-state materials for hydrogen storage [8–12]. Among the solid materials used to store hydrogen, magnesium-based compounds are well known for their abundance, low

cost, cycling stability, and high hydrogen storage capacity (approximately 7.6 wt%) [2,13–15]. However, magnesium hydride (MgH₂) releases hydrogen slowly and decomposes at elevated temperatures, often exceeding 360 °C at 0.1 MPa of pressure in an argon atmosphere, because of its remarkably high activation energy, which has been reported to exceed 152 kJ/mol [16–19].

Recent work has explored solar-driven strategies that couple photothermal heating with catalytic interfaces to reduce the external energy required for reversible storage in light-weight hydrides. For MgH₂, atomic-level reconstructions that integrate photothermal absorption and catalysis have enabled stable solar-driven cycling under concentrated irradiation by co-localizing light-induced heat and active sites [1]. Complementary concepts that employ photothermal MXene-based

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layers have also demonstrated fully solar-driven cycling of MgH_2 [18]. Beyond Mg-based systems, light-enabled hydrogen storage has been reported in borohydrides where photogenerated vacancies destabilize B–H bonds at near-ambient conditions [15]. In parallel with these light-assisted approaches, investigators have pursued thermally driven strategies that rely on nanostructuring of MgH_2 , the use of diverse catalysts, mechanical alloying, and the creation of multiphase composites [20,21]. Numerous elements have been incorporated into MgH_2 to boost its behavior in hydrogenation and dehydrogenation, including Zr, Fe, Mn, V, Cr, Ti, Nb, and Ni, among others [17]. Titanium and niobium have been utilized as catalysts in their metallic form, as well as in oxides, carbides, and other variations [22]. MXene refers to 2D transition metal carbonitrides, carbides, and nitrides. MXenes have been utilized in various applications, including microelectronics, nanoelectronics, supercapacitors, and electrocatalytic water splitting [23,24]. Titanium and niobium MXenes have been utilized as additives to boost the hydrogen storing characteristics of MgH_2 [9,25–27]. The two-dimensional structure and high surface area significantly enhance the MgH_2 hydrogenation and dehydrogenation behavior and lower the dehydrogenation temperature. Titanium MXene was produced by Zhu et al. [28]; the resulting MgH_2 -titanium MXenes composites exhibited a hydrogen desorption of 3 wt% at 150 °C in 2.5 h. Similarly, niobium MXenes have also been used as additives to improve the hydrogenation and dehydrogenation behavior of MgH_2 . Liang et al. [29] produced MgH_2 -niobium MXenes composites, which exhibited hydrogen desorption and absorption of approximately 6 and 7 wt% respectively at 200 °C in 6 min. Potassium hydride (KH) has recently emerged as an effective mechanochemical reductant for generating defect-rich suboxides from robust transition-metal oxides, thereby creating catalytically active interfaces relevant to MgH_2 [30]. Milling TiO_2 with KH produces “black” TiO_2 -x containing Ti^{3+} and oxygen-vacancy defects, and when used with MgH_2 it lowers the dehydrogenation onset to ~194 °C and enables rapid low-temperature cycling [31]. Fu et al. [32] developed a niobium-based bimetallic catalyst, CuNb_2O_6 , with exceptional catalytic performance. The $\text{CuNb}_2\text{O}_6/\text{MgH}_2$ composite can absorb 4.28 wt% of hydrogen in 10 min at 100 °C. Additionally, the composite can absorb approximately 2 wt% hydrogen within 60 min at 50 °C. For hydrogen desorption, the composite can desorb 4.65 wt% of hydrogen within 20 min at 225 °C. After 50 cycles at 300 °C, the capacity retention was 87%. Wang et al. [33] developed a composite of MgH_2 and CeO_2 -Ni-rGO. With the addition of 10 wt% CeO_2 -Ni-rGO, the MgH_2 composite achieves a hydrogen uptake of 4.0 wt% within 60 s at 100 °C. According to the authors, the hydrogenation activation energy decreases to 52.45 kJ/mol, and the onset of dehydrogenation temperature decreases to 195 °C. The MgH_2 and 10 wt% CeO_2 -Ni-rGO composite releases about 5 wt% of hydrogen in 5 min at 250 °C. After 30 hydrogen absorption/desorption cycles at 300 °C, the capacity retention was 97%. Liu et al. [34] developed a coral-like $\text{NiO}/\text{NiFe}_2\text{O}_4$ heterojunction catalyst. The MgH_2 - $\text{NiO}/\text{NiFe}_2\text{O}_4$ composite can release 6.2 wt% of hydrogen at 275 °C in 20 min. On the other hand, the composite can absorb 4.4 wt% of hydrogen in 30 min at 100 °C. According to the authors, the hydrogen desorption onset decreases to 188 °C, which represents a 133 °C difference compared to ball-milled MgH_2 . Besides, the activation energy decreases to 86.97 kJ/mol, representing a reduction of 62.17 kJ/mol relative to ball-milled MgH_2 .

Despite significant progress, current MgH_2 catalytic systems face persistent barriers that limit translation. State-of-the-art catalysts (most notably MXenes) remain largely non-commercial and are typically produced under restricted laboratory conditions with hazardous etchants and complex, laboratory-specific syntheses, which increases cost and limits scalability [35,36]. In parallel, mechanistic interpretations at metal/oxide-hydride interfaces continue to evolve, particularly regarding the roles of defect-rich suboxides and hydrogen spillover in lowering nucleation barriers and accelerating Mg–H bond dynamics [16, 26,37]. These constraints highlight a clear gap for catalyst solutions that couple strong kinetic benefits with industrial practicality, specifically,

derivation from commercial precursors and processing through scalable routes.

Motivated by this gap, the present work introduces a fully commercial catalyst system in which KH-modified $\text{TiO}_2/\text{Nb}_2\text{O}_5$ (CAT) is combined with carbon-coated Ni nanoparticles (C@Ni). We investigate how this catalyst, incorporated through two distinct routes—a one-step high-energy ball-milling method and a two-step mixing strategy—affects key performance metrics, including dehydrogenation onset temperature, hydrogen absorption and desorption kinetics, apparent activation energy, low-temperature hydrogen uptake, and cycling stability. By demonstrating these effects without relying on laboratory-specific synthesis routes, such as MXene fabrication, this study proposes a scalable and practical alternative for improving MgH_2 -based hydrogen storage materials.

2. Materials and methods

Magnesium hydride ($\geq 98\%$), TiO_2 nanoparticles (99.0%), and Nb_2O_5 powders (99.0%) were purchased from Lead Optima Element Tech Co. Carbon-coated nickel nanoparticles (C@Ni, $\geq 99.9\%$) were purchased from Nanostructured & Amorphous Materials. All samples were handled inside an argon-filled glovebox. (Vigor Tech USA), maintaining O_2 and H_2O levels less than one part per million. Potassium hydride (KH, 30 wt % dispersion in mineral oil) was purchased from Sigma-Aldrich. To remove the mineral oil, the KH was washed repeatedly in hexanes in an argon-filled glovebox. No further treatment was applied to any of the remaining powders. As-received magnesium hydride had a particle size of $8.19 \pm 7.44 \mu\text{m}$. TiO_2 nanoparticles had a particle size of $23.05 \pm 9.67 \text{ nm}$, with more than 80% measuring below 30 nm (see Fig. S1). Nb_2O_5 particles had a mean size of $154.69 \pm 74.30 \text{ nm}$, with over 70% smaller than 200 nm (see Fig. S2). The carbon-coated nickel nanoparticles had a particle size of $28.30 \pm 16.10 \text{ nm}$, with 75% of them being smaller than 40 nm (see Fig. S3).

The catalyst (CAT) was synthesized by mixing TiO_2 , Nb_2O_5 , and KH in equal molar ratios (1:1:1), following the stoichiometry reported by Dai et al. [31]. In this configuration, KH serves to pre-induce defect-rich Ti/Nb suboxides within the commercial KH- TiO_2 - Nb_2O_5 precursor. This approach offers a scalable synthesis route for generating highly active oxide–metal interfaces. The mix was ball-milled in a Retsch Emax high-energy ball mill with a ball-to-powder weight ratio (BPR) of 40:1, 50% of filling vial percentage, and 3 mm ZrO_2 balls in a 125 mL stainless steel jar coated with ZrO_2 at 400 RPM. Ball milling was carried out for 8 h in cycles of 20 min milling followed by 5 min cooling. No additional post-treatment was applied to the CAT after milling. The as-milled powder was collected and stored in the glovebox. The CAT and the C@Ni were incorporated to the MgH_2 by two methods, as displayed in Fig. 1. The first method involves a single step of ball milling of all components (MgH_2 , CAT, and the C@Ni). The ball milling was performed in the high-energy ball mill employing a 125 mL stainless steel jar coated with ZrO_2 , with 3 mm ZrO_2 balls, a BPR of 80:1 and a 50% filling vial percentage. The ball milling process lasted one hour, with 10-minute intervals of ball milling, followed by 10 min of rest. The second method consisted of two steps. In the first step, the CAT and MgH_2 are ball-milled under the same conditions as those explained in the first method. Following that, in the second step, we used a high-energy ball mill set at 800 RPM for one hour to combine 400 mg of the ball-milled sample with C@Ni, without grinding bodies, in a 50 mL stainless steel jar coated with ZrO_2 . Hereafter, BM and MIX are the abbreviations for the first and the second method, respectively. For comparison, MgH_2 subjected to ball milling without CAT or C@Ni (hereafter referred to “as-milled MgH_2 ”) was used. In our previous work [2], the MIX and BM methods were systematically evaluated using C@Ni as the additive, and the optimal additive content for each method was independently determined. Accordingly, the C@Ni loading used in both MIX and BM routes was selected on the basis of those experimental results.

Information about morphological and compositional

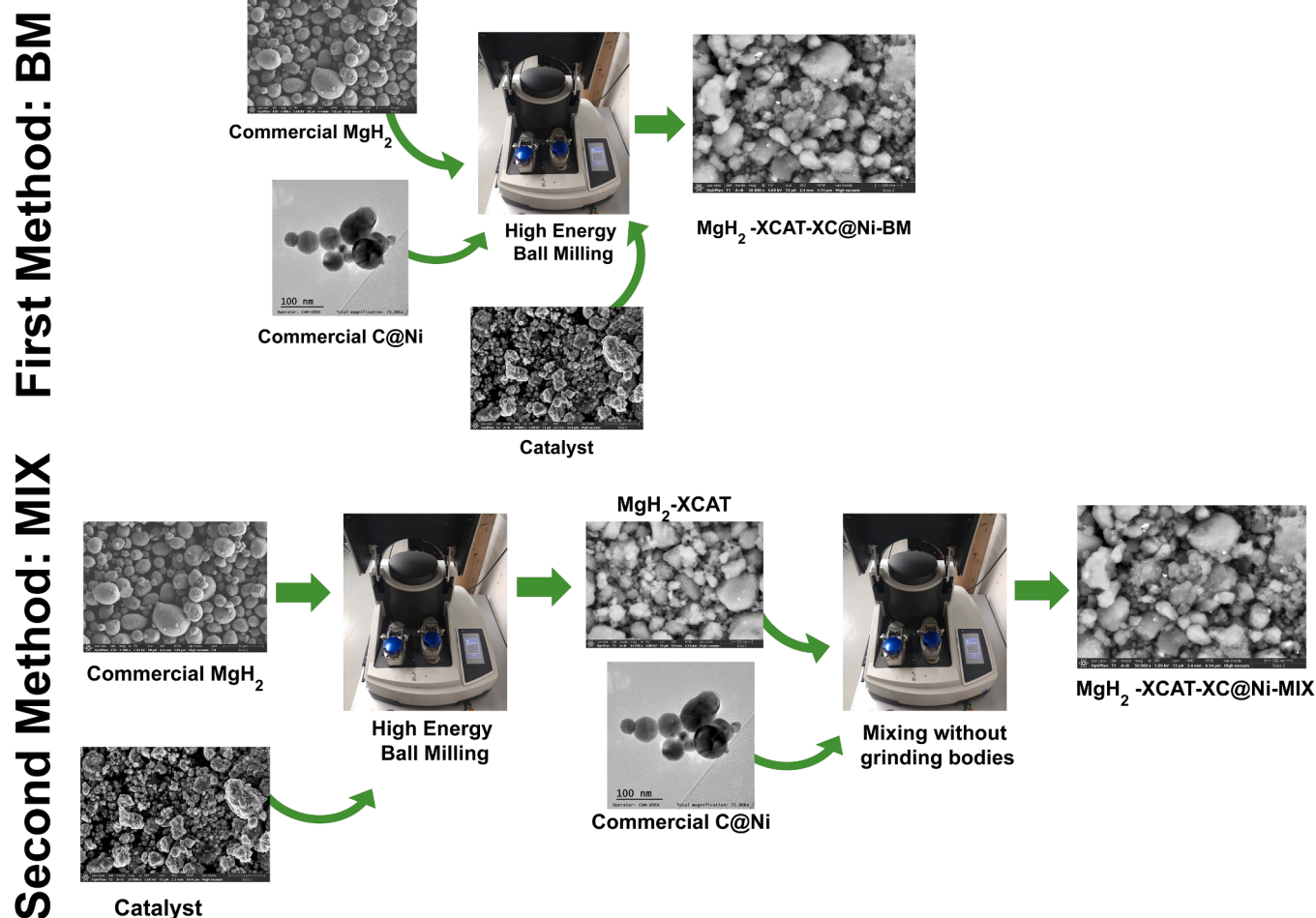


Fig. 1. Methods for adding the catalyst and the C@Ni to MgH_2 .

characterization, as well as hydrogen storage assays, is provided in [supplementary information](#). More details about the self-designed Sievert-type apparatus could be found in [38].

3. Results

Fig. 2 presents the SEM image and EDS elemental mapping of the catalyst. The catalyst particles are predominantly 200 and 300 nm in size and form agglomerates of approximately 1–2 μm . The EDS maps further confirm a uniform spatial distribution of Ti, K, O, and Nb throughout the catalyst, indicating effective mixing and homogenization during the milling. Elemental composition from EDX of CAT is shown in Table S1. The XPS spectra of the catalyst are shown in Fig. 3. In the C 1s–K 2p region (Fig. 3a), four characteristic peaks are identified. The signals at 285 eV and 288.45 eV correspond to C–C and C=O bonding, respectively, whereas the peaks at 292.78 eV and 295.57 eV are associated with K–O species [39,40]. In the Nb 3d region (Fig. 3b), three fitted peaks are observed. The peaks at 206.59 eV (Nb 3d_{5/2}) and 209.30 eV (Nb 3d_{3/2}) are attributed to Nb⁴⁺–O bonding [41–43]. Whereas the intermediate peak at 207.56 eV is consistent with Nb⁵⁺–O species [41]. Similarly, the Ti 2p region (Fig. 3c) displays three well-resolved contributions. The peaks at 457.89 eV (Ti 2p_{3/2}) and 463.79 eV (Ti 2p_{1/2}) correspond to Ti³⁺ states, whereas the peak at 458.30 eV is assigned to Ti⁴⁺ (Ti 2p_{3/2}) [44–48]. Regarding the O 1s region (Fig. 3d), three distinct contributions are identified at 532.85, 530.98, and 529.40 eV. The peak at 532.85 eV is related to surface hydroxyl groups [49,50]. On the other hand, the peak at 530.98 eV is attributed to non-stoichiometric oxide species (O_{NS}), which are typically

associated with the reduced Ti³⁺ and Nb⁴⁺ states present in the catalyst. In contrast, the peak at 529.40 eV corresponds to lattice oxygen (O_{L}), originating from fully oxidized Ti⁴⁺ and Nb⁵⁺ species [43,45,47,51–53]. The relative integrated areas of these components yield an $\text{O}_{\text{NS}}/\text{O}_{\text{L}}$ ratio of 2.46, indicating a highly defective oxide surface enriched in non-stoichiometric oxygen species.

Fig. 4 shows the HRTEM images of the catalyst together with their corresponding FFT patterns, and the measured d -spacings are summarized in Table S2. Several observed d -spacing values exceed 0.3509 nm, which is the largest interplanar distance reported for TiO₂ polymorphs (specifically the anatase (011) plane) [54–56]. These enlarged spacings therefore indicate the presence of titanium suboxides. Additional d -spacing values match well with those expected for niobium suboxides, such as NbO and NbO₂. Furthermore, the spacings greater than 0.6 nm are consistent with complex niobium suboxides, particularly Nb₁₂O₂₉, suggesting that KH reduction promotes the generation of highly defective and sub-stoichiometric oxide phases within the catalyst.

The SEM images and EDS elemental mapping of the MgH_2 –3 wt% CAT–3 wt% C@Ni–MIX composite are presented in Fig. 5. As shown in Fig. 5 and Fig. S4, the incorporation of CAT and C@Ni does not produce significant changes in particle size of MgH_2 , indicating that the milling and mixing steps do not induce substantial morphological changes of the hydride matrix. Moreover, the homogeneous distribution of Ti, K, Ni, and Nb observed in the EDS maps confirms a uniform dispersion of both the catalyst and the carbon-coated Ni nanoparticles throughout the MgH_2 particles. Similar results were obtained from the SEM micrographs and EDS mapping of the MgH_2 –1 wt% CAT–0.5 wt% C@Ni–BM composite (See Figs. S4 and S5). Importantly, no Zr-related signals were

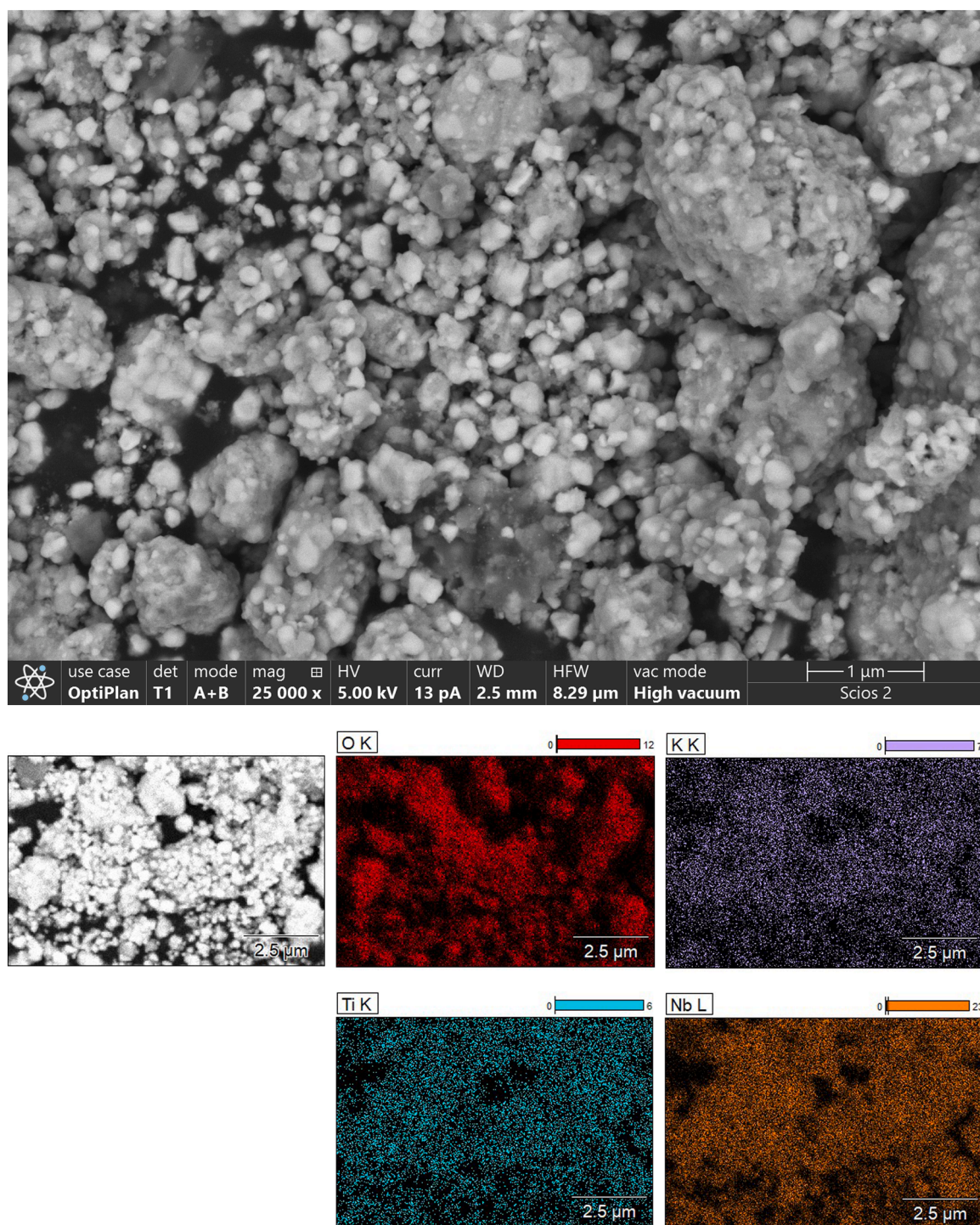


Fig. 2. SEM images and EDS mapping analysis of the catalyst. Oxygen is red, potassium is violet, titanium is cyan, and niobium is orange in the EDS mapping study.

detected in the EDS spectra, despite the use of ZrO_2 grinding media and ZrO_2 -coated milling jars. This confirms that no contamination from the milling equipment was introduced into the final material. It is important to note, however, that SEM-EDS provides areal or volumetric information rather than surface-specific measurements. It cannot distinguish nanoparticles exposed at the outer surface from those that are partially embedded within MgH_2/CAT agglomerates, and it cannot quantify the fraction of catalytically accessible Ni near the surface. In addition, the finite interaction volume and peak overlaps limit nanoscale resolution and the quantification of light elements, for example the carbon shells, and EDS cannot resolve the chemical state of nickel (e.g., Ni^0 versus

NiO). Consequently, although the maps confirm compositional homogeneity and rule out phase segregation or core-shell morphologies at the microscale, they do not directly establish the surface accessibility of $\text{C@Ni}/\text{CAT}$ sites. This limitation probably differentiates the BM and MIX routes and underpins the superior low-temperature hydrogen uptake observed for MIX. Direct quantification of exposed active sites will require surface-sensitive and nanoscale analyses beyond SEM-EDS.

The TPD curves obtained at a heating rate of 5°C min^{-1} are shown in Fig. 6, and the corresponding onset temperatures, DSC peak temperatures, activation energies, and hydrogen capacities at 300, 275, and 260°C are summarized in Table 1. Incorporating CAT and C@Ni

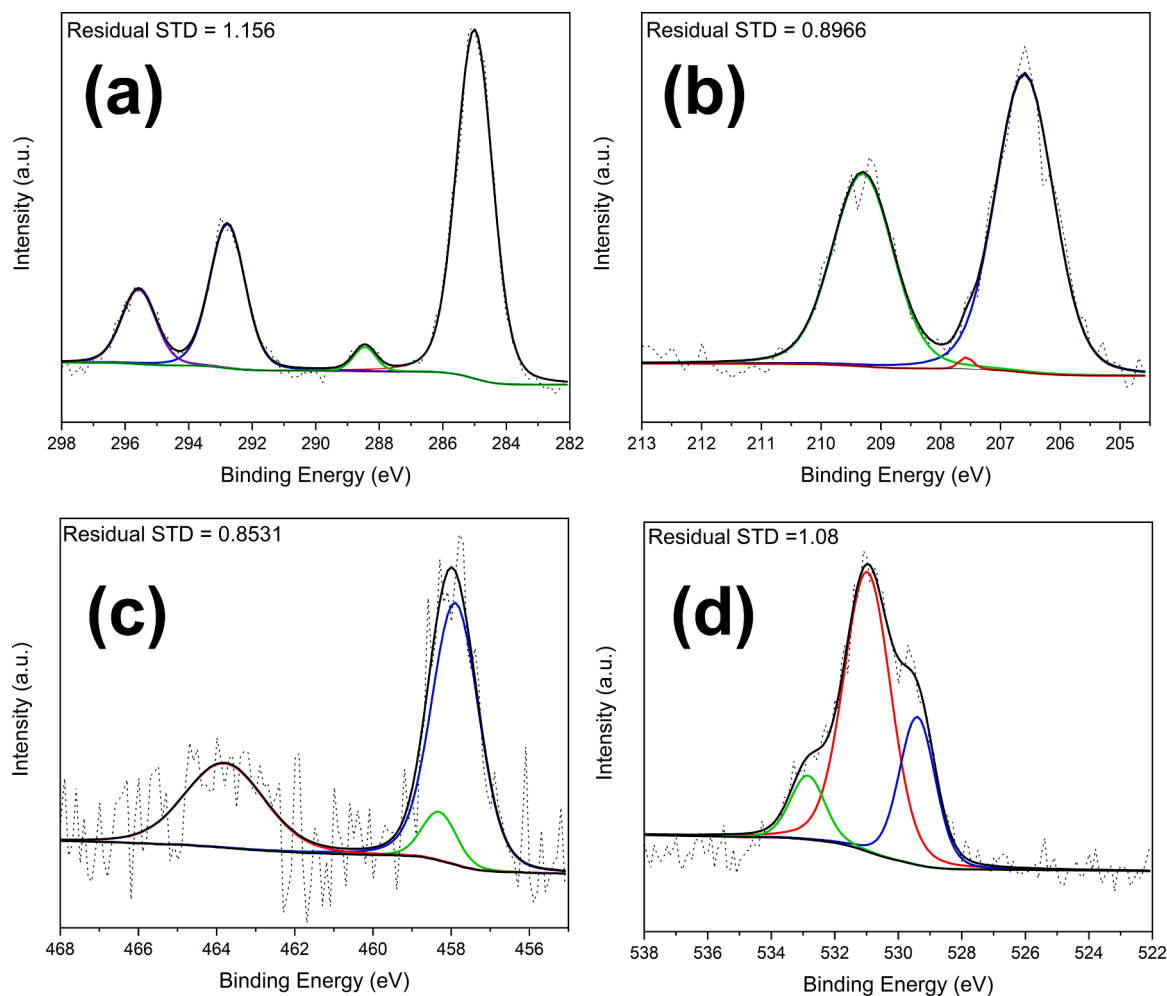


Fig. 3. X-ray photoelectron spectroscopic spectra of the catalyst. C 1 s – K 2p region (a), Nb 3d region (b), Ti 2p region (c), O 1 s region (d).

significantly decreases the dehydrogenation onset temperature of MgH_2 , reducing it from 321 °C for the as-milled MgH_2 to below 236 °C in all catalyst-containing samples (Fig. 6, Table 1). This reduction demonstrates the strong catalytic influence of the KH-modified $\text{TiO}_2/\text{Nb}_2\text{O}_5$ phases and the carbon-coated Ni nanoparticles.

The DSC profiles for samples with and without CAT and C@Ni, also recorded at 5 °C min⁻¹, are presented in Fig. 7. As shown in Fig. 7 and Table 1, the addition of the catalyst system leads to a decrease of at least 9 °C in the DSC peak temperature relative to the as-milled MgH_2 , with the most pronounced shift reaching 32 °C. These collective results confirm that the introduction of CAT and C@Ni effectively destabilizes Mg–H bonding and lowers the temperature required for hydrogen release.

Fig. 8 shows the isothermal hydrogen desorption and absorption kinetics of the CAT- and C@Ni-containing samples at 300, 275, and 260 °C. When compared with the as-milled MgH_2 , the catalytic effect is apparent. At 300 °C, the as-milled MgH_2 requires approximately 200 min to reach 6.5 wt% hydrogen desorption (Fig. S6), whereas the MgH_2 –3 wt% CAT–0.5 wt% C@Ni–BM composite achieves 6.45 wt% in only 20 min (Table 1). In terms of hydrogen absorption at this temperature, all catalyst-containing samples exhibit rapid uptake, reaching approximately 6.1 wt% within 5 min.

At 275 °C, the MgH_2 –1 wt% CAT–0.5 wt% C@Ni–BM sample demonstrates the best dehydrogenation performance, releasing 4.72 wt% hydrogen in 40 min, while the remaining compositions desorb between 4.1 and 4.5 wt% under the same conditions. Hydrogen absorption at 275 °C is likewise fast for all samples, with values close to 6 wt%

achieved in approximately 8 min.

At 260 °C, all composites desorb around 2.7 wt% hydrogen within 60 min, except for the MgH_2 –1 wt% CAT–3 wt% C@Ni–MIX sample, which reaches 2.4 wt%. Hydrogen absorption at this temperature also proceeds efficiently across the samples, reaching $\approx$ 6 wt% within 10 min, except for MgH_2 –3 wt% CAT–3 wt% C@Ni–MIX, which attains 5.84 wt% under the same conditions.

Hydrogen absorption at 150 °C was evaluated for all samples over 50 min (Fig. 9). Under these conditions, the MgH_2 –1 wt% CAT–3 wt% C@Ni–MIX composite exhibits the highest performance, absorbing 5.77 wt% hydrogen, whereas the remaining samples reach 3.80 wt% or less. This result highlights the superior low-temperature activity of the MIX-processed material.

Fig. 10 presents the isothermal absorption kinetics of the MgH_2 –1 wt% CAT–3 wt% C@Ni–MIX sample at 150, 100, and 75 °C. Notably, this material maintains significant hydrogen uptake even at substantially lower temperatures, absorbing 4.28 wt% at 100 °C and 3.47 wt% at 75 °C within 120 min, demonstrating exceptional catalytic efficiency for low-temperature hydrogenation.

Cycling stability was assessed at 300 °C for the MgH_2 –1 wt% CAT–0.5 wt% C@Ni–BM composite (Fig. 11). After 20 cycles, the sample retains a reversible desorption capacity of 5.07 wt% (corresponding to a 78.72% retention) and a reversible absorption capacity of 5.22 wt% (78.77% retention). These results confirm that the catalyst system enhances hydrogen sorption kinetics without compromising cycling durability.

The JMAK and Arrhenius plots for all evaluated samples are

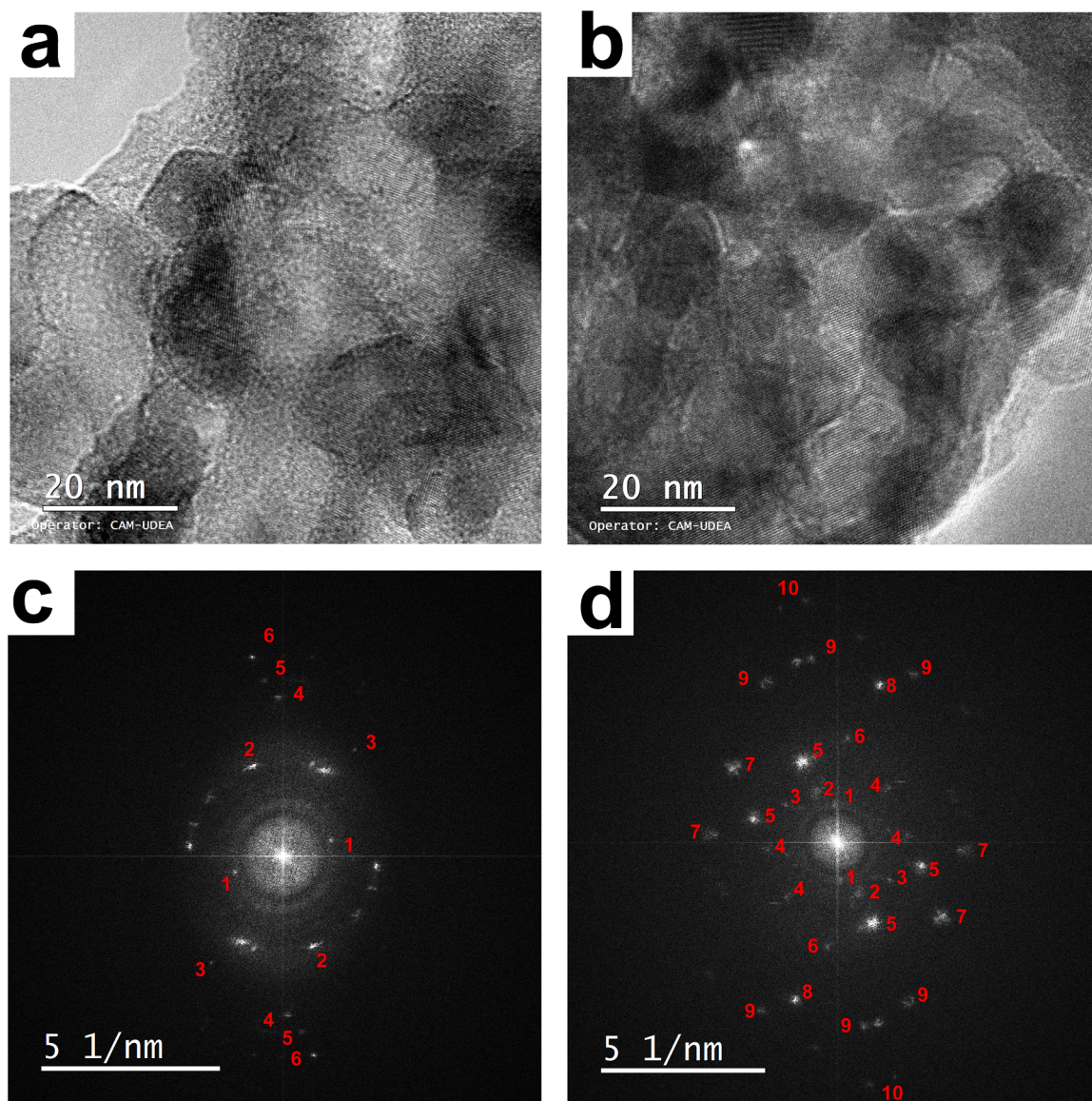


Fig. 4. High-resolution TEM ((a), (b)) and associated FFT patterns ((c), (d)) of the catalyst (CAT), highlighting lattice fringes and reciprocal-space features.

presented in Fig. 12, and the corresponding activation energies (E_a) derived from these analyses are summarized in Table 1. As shown in Fig. 12 and Table 1, every catalyst-containing sample exhibits a substantial lower E_a than as-milled MgH_2 . In all cases, the activation energy decreases by at least 44 kJ mol^{-1} relative to the reference material (Fig. S7), confirming the strong catalytic effect of the KH-modified $\text{TiO}_2/\text{Nb}_2\text{O}_5$ phases and the carbon-coated Ni nanoparticles on dehydrogenation kinetics. Among all compositions, the MgH_2 -3 wt% CAT-3 wt% C@Ni-MIX sample displays the lowest activation energy, highlighting the enhanced efficiency of the MIX incorporation method in promoting faster hydrogen sorption pathways.

Fig. 13 presents the SEM images of the MgH_2 -1 wt% CAT-0.5 wt% C@Ni-BM composite after the cycling tests. As observed, the particle size distribution becomes non-uniform after repeated hydrogenation-dehydrogenation cycles: some particles range from 1 to $4 \mu\text{m}$, whereas others are smaller than $1 \mu\text{m}$. At higher magnification, the larger agglomerates are revealed to consist of nanometric sub-particles ($< 50 \text{ nm}$), indicating progressive fragmentation and reagglomeration during cycling. This multiscale morphology is typical of MgH_2 systems subjected to repeated volumetric expansion and contraction, and it is consistent with the moderate capacity retention observed for this

sample.

4. Discussion

According to the TPD curves, the MIX-processed samples exhibit onset temperatures approximately 12°C lower than their BM counterparts. Moreover, all compositions incorporating CAT and C@Ni show a marked reduction in the dehydrogenation onset temperature relative to the as-milled MgH_2 , confirming the strong catalytic effect of the combined KH-modified oxides and carbon-coated Ni nanoparticles. A similar trend is observed in the DSC measurements: samples containing CAT and C@Ni display a substantial decrease in the DSC peak temperature when compared with as-milled MgH_2 , further demonstrating that the catalyst system effectively destabilizes the Mg-H bond and facilitates earlier hydrogen release.

These results are consistent with previous findings by Dai et al. [31], who synthesized black TiO_2 through KH-assisted ball milling and used it to enhance the hydrogenation-dehydrogenation behavior of MgH_2 . Their material exhibited a TPD onset temperature of 194°C at a heating rate of 2°C min^{-1} , representing a 96°C reduction relative to their reference MgH_2 sample. The agreement between these earlier

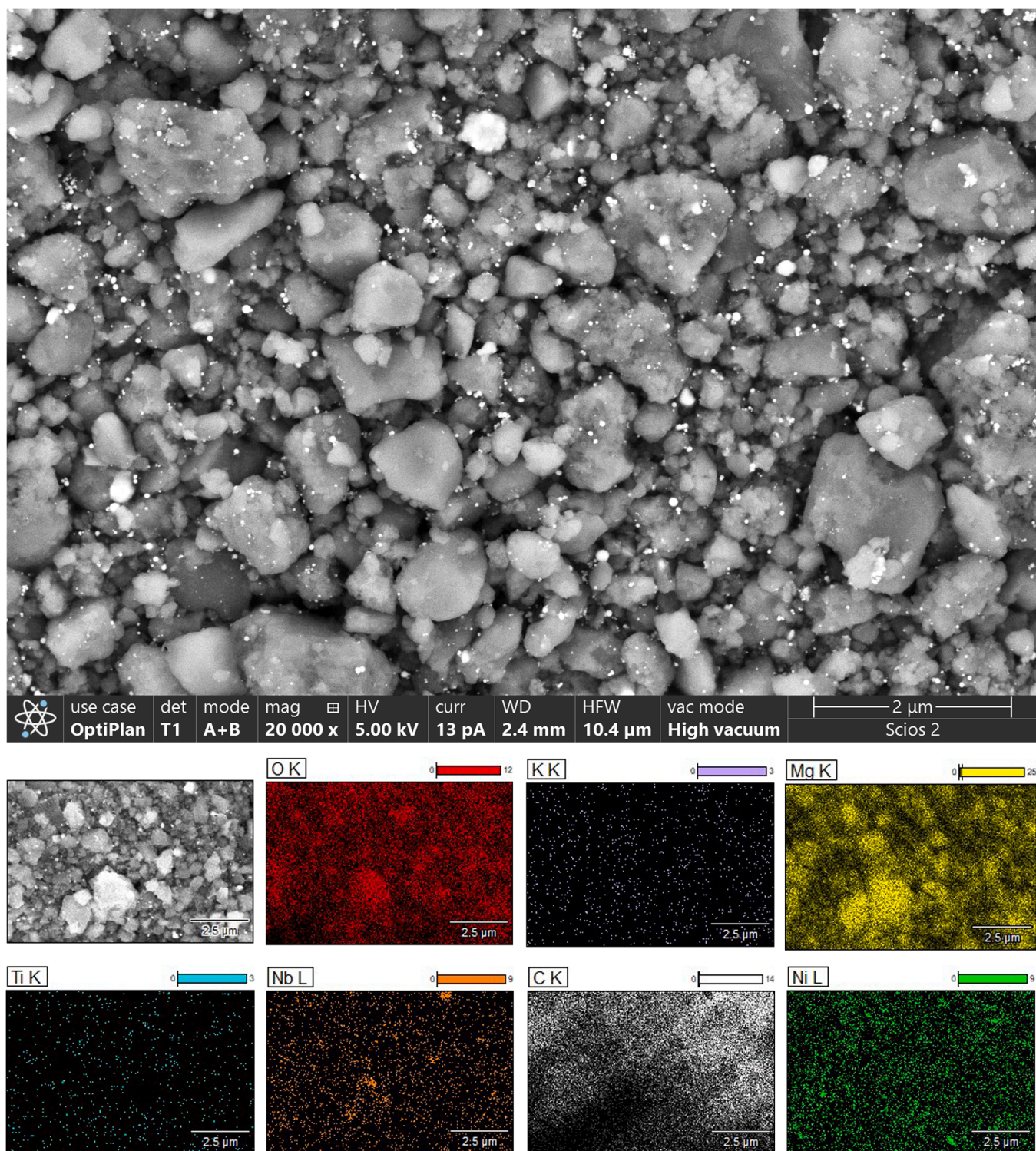


Fig. 5. SEM micrographs and EDS mapping of the MgH_2 -3 wt% CAT-3 wt% C@Ni-MIX composite. Elemental distribution is represented as follows: O (red), K (violet), Mg (yellow), Ti (cyan), Nb (orange), C (white), and Ni (green).

observations and the present results reinforces the role of KH-induced oxide reduction (including the formation of Ti^{3+} / Nb^{4+} species), significantly promoting hydrogen sorption kinetics in MgH_2 -based systems.

At 300, 275, and 260 °C, both MIX and BM samples display excellent dehydrogenation behavior, particularly in terms of their reduced activation energies and accelerated hydrogen desorption kinetics. Notably, particular attention should be given to the performance of the

MgH_2 -1 wt% CAT-3 wt% C@Ni-MIX sample, which exhibits remarkable low-temperature hydrogen absorption. This composite absorbs 5.77 wt% hydrogen in 50 min at 150 °C, and remains active even at significantly lower temperatures, reaching 4.28 wt% at 100 °C and 3.47 wt% at 75 °C. These results highlight the exceptional catalytic efficiency of the MIX-processed material under low-temperature hydrogenation conditions.

Table 2 compares the hydrogen storage performance obtained in this

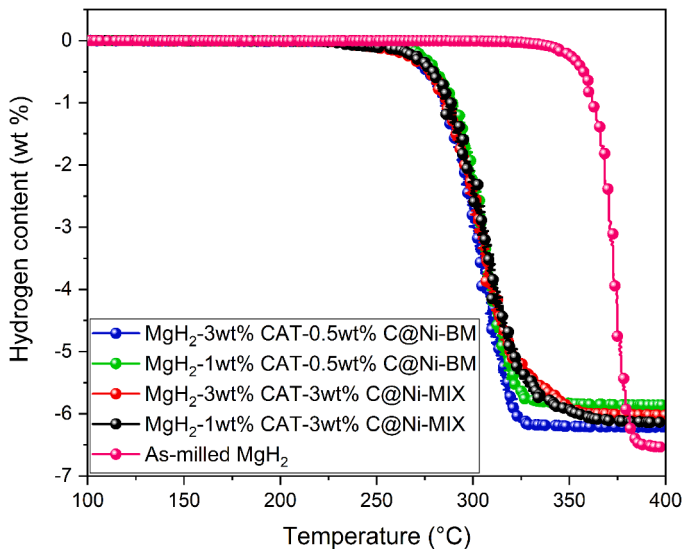


Fig. 6. Temperature-programmed desorption (TPD) curves of the evaluated samples, recorded at a heating rate of 5 °C min⁻¹.

work with values previously reported in the literature. Among the cited studies, MgH₂-Nb-MXene composites stand out for achieving rapid hydrogen desorption, approximately 6 wt% at 200 °C in 6 min. However, despite their excellent kinetics, these materials have notable drawbacks: MXenes are not commercially available, and their synthesis typically requires hydrofluoric acid, a highly corrosive and hazardous reagent [26,29]. These limitations hinder scalability and practical deployment. In contrast, most MgH₂-based hydrogen storage materials reported in the literature are evaluated at temperatures above 280 °C, and their catalytic additives are often produced via specialized laboratory synthesis routes that involve controlled atmospheres, multi-step procedures, or non-commercial precursors. The approach employed in the present study differs fundamentally from these strategies. Here, the catalyst system was synthesized exclusively from commercially available powders (KH, TiO₂ nanoparticles, Nb₂O₅ nanoparticles, and carbon-coated Ni nanoparticles) yet delivers competitive performance at lower additive loadings. For example, the MgH₂-1 wt% CAT-0.5 wt% C@Ni-BM composite achieves ~2.5 wt% hydrogen desorption at 260 °C

in 1 h, demonstrating the catalyst effectiveness even at minimal loading. Furthermore, when comparing these results with our previous study [2], which evaluated only commercial carbon-coated Ni nanoparticles, the beneficial effect of incorporating CAT becomes clear. In the earlier work, the best-performing materials desorbed hydrogen at 275 °C and absorbed hydrogen at 150 °C, whereas in the present study, the optimized composites can desorb at 260 °C and absorb at temperatures as low as 75 °C. This improvement highlights the synergistic effect between KH-modified TiO₂/Nb₂O₅ and C@Ni and underscores the novelty and practical relevance of using a fully commercial, scalable catalyst system to improve MgH₂ hydrogen storage performance.

Pure MgH₂ is well known for limited cycling stability, with capacity retention often falling below 70% under repeated hydrogenation–dehydrogenation cycles [67]. Other studies report slightly improved behavior, such as 82% retention after only five cycles, which still highlights the intrinsic degradation issues associated with MgH₂-based materials [68]. In contrast, the MgH₂-1 wt% CAT-0.5 wt% C@Ni-BM composite developed in this work exhibits an enhanced

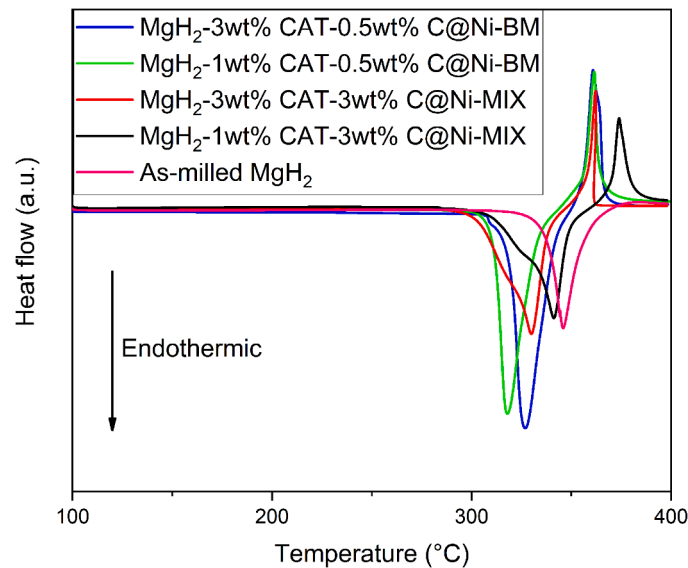


Fig. 7. Differential scanning calorimetry (DSC) curves recorded at 5 °C min⁻¹.

Table 1

Onset temperature from TPD, lowest peak temperature from DSC, and Activation Energy of all samples.

Sample	Onset dehydrogenation temperature from TPD (°C)	Temperature at DSC Peak (°C)	Activation Energy (Ea) (kJ/mol)	Hydrogen content at 300 °C. Dehydrogenation/ Hydrogenation (wt%)	Hydrogen content at 275 °C. Dehydrogenation/ Hydrogenation (wt%)	Hydrogen content at 260 °C. Dehydrogenation/ Hydrogenation (wt%)
MgH ₂ -3 wt % CAT-0.5 wt% C@Ni-BM	234.24	326.90	97.9 ± 2.7	6.45/6.22	4.16/6.16	2.63/6.22
MgH ₂ -1 wt % CAT-0.5 wt% C@Ni-BM	235.06	317.92	108.1 ± 6.6	6.44/6.13	4.72/6.08	2.77/6.04
MgH ₂ -3 wt % CAT-3 wt% C@Ni-MIX	218.13	329.93	100.5 ± 6.3	5.73/6.22	4.56/6.29	2.71/6.01
MgH ₂ -1 wt % CAT-3 wt% C@Ni-MIX	220.60	341.20	93.8 ± 10.0	5.62/6.12	4.14/6.11	2.36/5.84
Ball-milled MgH ₂	321.59	350.40	152.5 ± 15.29	6.5/6.5	—	—

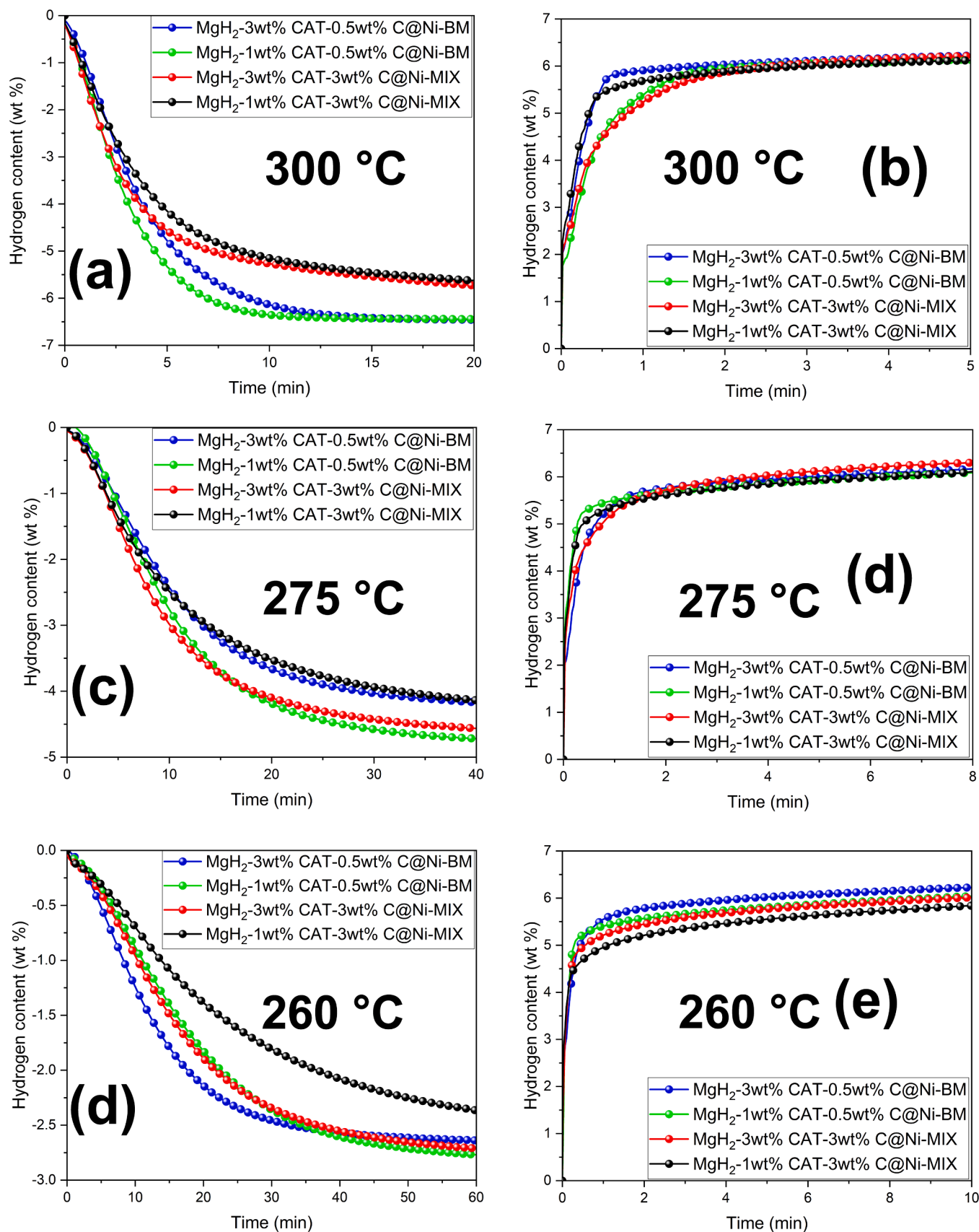


Fig. 8. Isothermal kinetics curves for hydrogen desorption at 300 °C (a), 275 °C (c), and 260 °C (e), and hydrogen absorption at 300 °C (b), 275 °C (d), and 260 °C (f).

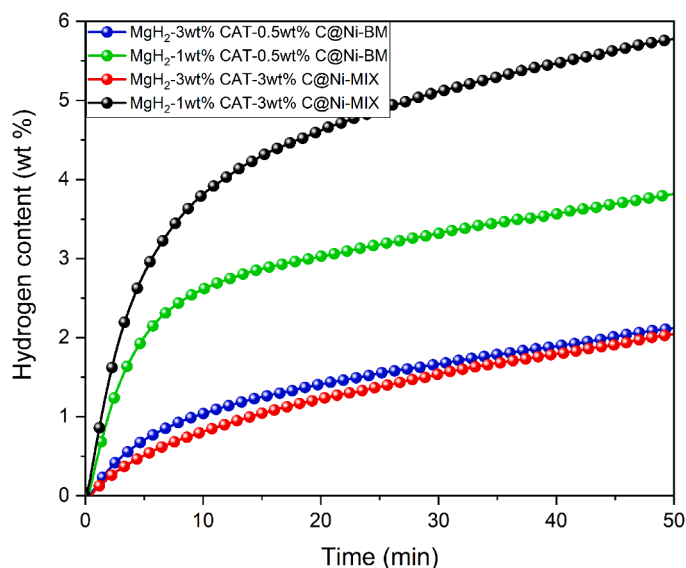


Fig. 9. Isothermal hydrogen absorption profiles of the samples at 150 °C.

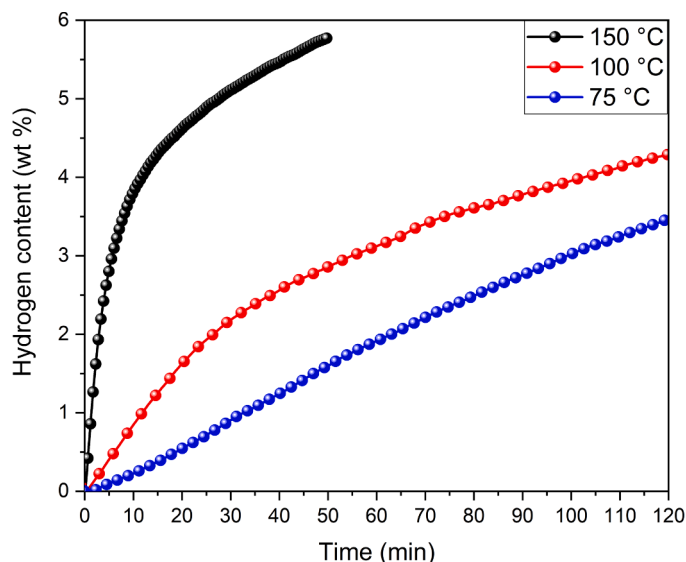


Fig. 10. Isothermal absorption profiles of the MgH₂-1 wt% CAT-3 wt% C@Ni-MIX sample at 150, 100, and 75 °C.

cyclability, maintaining a dehydrogenation capacity of 78.72% after 20 cycles. This performance is comparable to previously reported catalyst-modified systems [26,37,69,70], demonstrating that the combination of KH-modified oxides and carbon-coated Ni nanoparticles mitigates structural and kinetic degradation during long-term cycling. The decrease in hydrogen capacity during both desorption and absorption may be attributed to particle coarsening and agglomeration, which reduce the available surface area and thereby limit hydrogen diffusion (see Fig. 13) [71]. Another possible cause is the redistribution of catalytically active species like C@Ni or defect-rich Ti/Nb suboxides, due to particle coarsening and agglomeration, which reduces catalytic efficiency [71,72].

From the XPS analysis (Fig. 3), signals corresponding to Nb⁴⁺, Ti³⁺, and K-O bonding are clearly resolved. The presence of K-O species indicates the chemical transformation of KH during the milling process, consistent with the formation of non-stoichiometric oxides and oxygen-vacancy-rich phases (see Equations S1 and S2). According to the literature, such mixed-oxide systems often enhance hydrogen storage

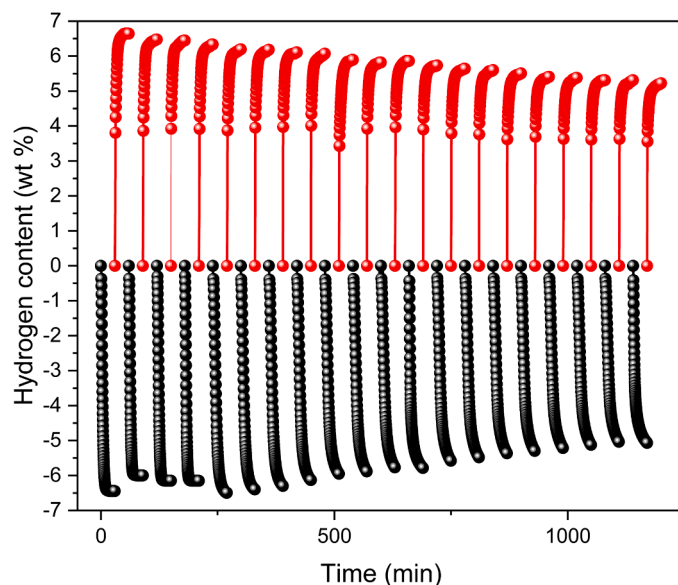


Fig. 11. Hydrogen desorption and absorption cycle curves at 300 °C for the MgH₂-1 wt% CAT-0.5 wt% C@Ni-BM material.

performance by providing active sites that facilitate both hydrogen absorption and desorption [30,31]. Furthermore, the reduction of TiO₂ and Nb₂O₅ by KH promotes the formation of titanium and niobium suboxides, as confirmed by both XPS and HRTEM analyses. These defects play a crucial role in modifying the surface electronic structure, improving charge transport, and enhancing catalytic activity of the resulting oxide phases [73]. Titanium and niobium suboxides are also known to facilitate H₂ dissociation, hydrogen spillover, and the subsequent release and uptake of hydrogen in MgH₂, thereby accelerating both hydrogenation and dehydrogenation kinetics by acting as highly reactive catalytic sites [74–76]. In addition, the catalytic effect of carbon-coated Ni nanoparticles (C@Ni) on MgH₂ sorption kinetics has been extensively detailed in our previous work [2], where Ni-assisted hydrogen activation and spillover mechanisms were shown to enhance MgH₂ performance significantly. The present results further reveal a synergistic interaction between the KH-modified oxide catalyst (CAT) and C@Ni, enabling hydrogen desorption below 275 °C and hydrogen absorption at temperatures as low as 75 °C. This synergy demonstrates the combined benefits of defect-rich oxide phases and Ni-mediated hydrogen activation, reinforcing the effectiveness of this fully commercial and scalable catalyst system.

SEM/EDS data indicate compositional homogeneity for both routes (Figs. 5 and S5), yet the microstructural scenarios they create differ. In BM, simultaneous high-energy milling of MgH₂, CAT, and C@Ni can partially embed C@Ni within MgH₂/CAT agglomerates and promote local coalescence, which reduces the fraction of Ni accessible at the surface. In MIX, the second mixing step, performed without grinding media, preserves the integrity of C@Ni and favors its deposition at the surface near defect-rich Ti/Nb suboxides, as supported by XPS of CAT and HRTEM *d*-spacings data. The resulting microstructure increases the density of exposed dissociation and spillover sites while shortening hydrogen diffusion paths. This picture consistently explains the observed kinetic trends. MIX composites show lower TPD onsets (218.1–220.6 °C) than their BM counterparts (234.2–235.1 °C, Fig. 6) and reach the lowest apparent activation energy ($E_a = 93.8 \pm 10.0$ kJ mol⁻¹, Fig. 12), while both routes decrease the DSC peak temperature relative to as-milled MgH₂ (Fig. 7). Consistent with enhanced near-surface exposure of Ni, MIX delivers superior low-temperature hydrogenation, reaching 5.77 wt% at 150 °C in 50 min and remaining active down to 100 °C with 4.28 wt% in 120 min and 75 °C with 3.47 wt % in 120 min (Figs. 9–10). Taken together, these results establish a

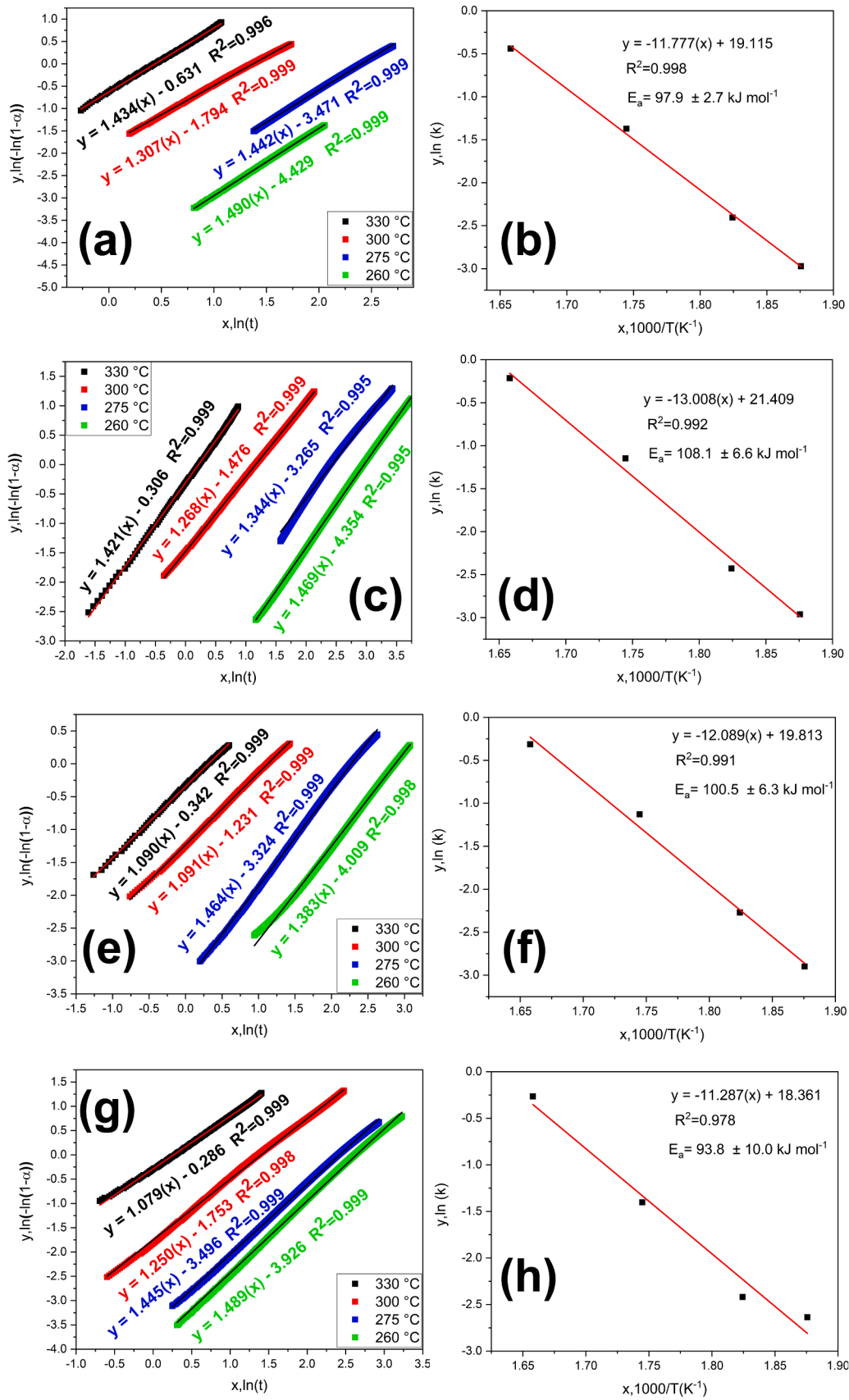


Fig. 12. JMAK plots of $\text{MgH}_2\text{-3wt\% CAT- 0.5 wt\% C@Ni-BM}$ (a), $\text{MgH}_2\text{-1wt\% CAT- 0.5 wt\% C@Ni-BM}$ (c), $\text{MgH}_2\text{-3wt\% CAT- 3 wt\% C@Ni-MIX}$ (e), $\text{MgH}_2\text{-3wt\% CAT- 3 wt\% C@Ni-MIX(g)}$ (g). Arrhenius plots of $\text{MgH}_2\text{-3wt\% CAT- 0.5 wt\% C@Ni-BM}$ (b), $\text{MgH}_2\text{-1wt\% CAT- 0.5 wt\% C@Ni-BM}$ (d), $\text{MgH}_2\text{-3wt\% CAT- 3 wt\% C@Ni-MIX}$ (f), $\text{MgH}_2\text{-3wt\% CAT- 3 wt\% C@Ni-MIX(g)}$ (h).

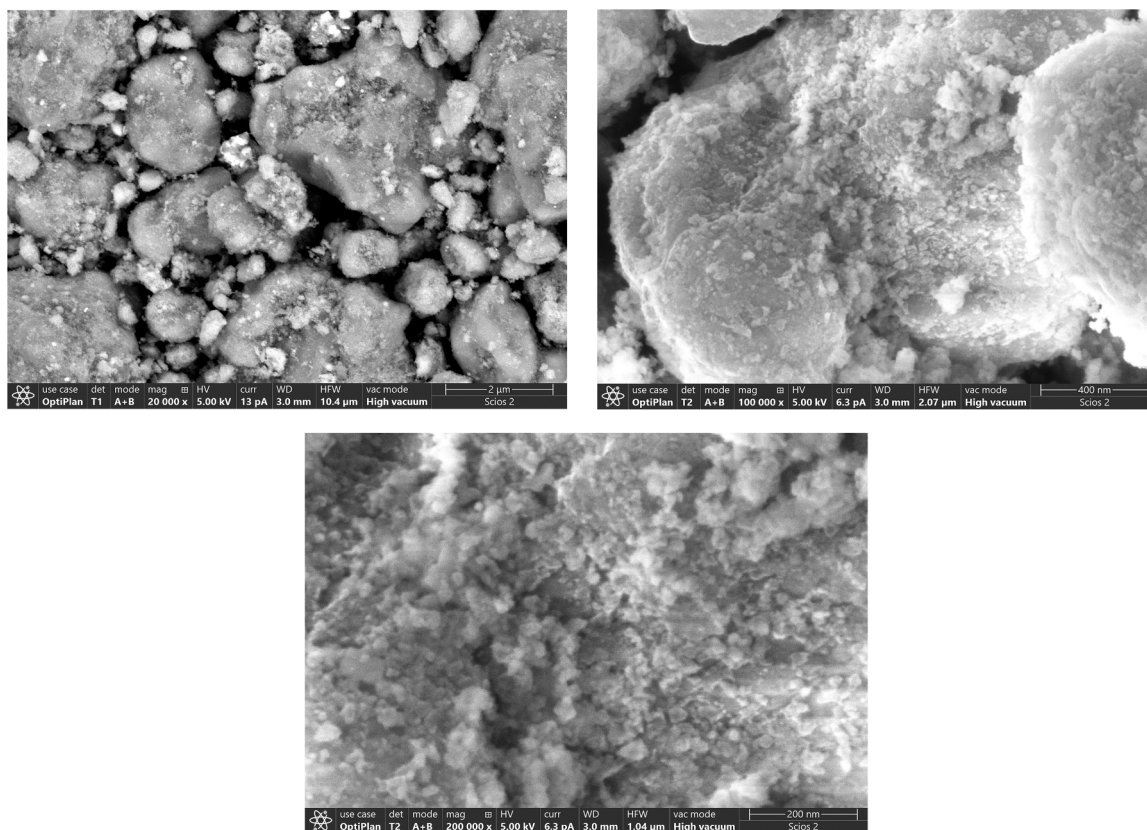


Fig. 13. SEM micrographs of MgH₂-1 wt% CAT-0.5 wt% C@Ni-BM after 20 hydrogenation-dehydrogenation cycles.

Table 2

Comparative summary of hydrogen-storage metrics from this study and previously reported MgH₂-based composites.

Additives	Activation energy for hydrogen desorption (kJ/mol)	Lower dehydrogenation temperature, time, and hydrogen content	Hydrogenation temperature, time, and hydrogen content	Reference
MgH ₂ -1 wt% CAT- 3 wt% C@Ni-MIX	93.8	260 °C, 60 min, 2.36 wt%	150 °C, 50 min, 5.77 wt%	This work
MgH ₂ -1 wt% CAT- 0.5 wt% C@Ni-BM	108.1	260 °C, 60 min, 2.77 wt%	150 °C, 50 min, 3.80 wt%	This work
TiO ₂ Quantum Dots	—	300 °C, 4.5 min, 6 wt%	100 °C, 30 min, 5 wt%	[57]
Nb ₂ O ₅ hollow spheres	101	250 °C, 20 min, 4 wt%	200 °C, 20 s, 5 wt%	[58]
Black TiO ₂ (K-TiO _{2-x})	69.1	260 °C, 60 min, 3 wt%	Room temperature, 6 h, 5 wt%	[31]
CuMoO ₄	110.2	325 °C, 10 min, 6.03 wt%	200 °C, 60 min, 5.7 wt%	[59]
Ni nanoparticles dispersed on porous hollow carbon nanospheres	98	250 °C, 30 min, 6.2 wt%	150 °C, 250 s, 5.7 wt%	[60]
flower-shaped niobium nitride (NbN) and 2D titanium carbide (Ti ₃ C ₂) (MXene)	44.8	300 °C, 180 s, 5.9 wt%	100 °C, 60 min, 5.8 wt%	[61]
Nano-Carbon supported CeO ₂ nanoparticles	101.9	320 °C, 50 min, 5.9 wt%	320 °C, 2 min, 5.6 wt%	[62]
Ni-MOF@Pd	34.6	250 °C, 50 min, 1 wt%	150 °C, 300 s, 6.1 wt%	[63]
Hydrangea-like NiO@KNbO ₃	71.8	285 °C, 50 min, 4.2 wt%	150 °C, 5 min, 4.95 wt%	[64]
KNbO ₃	104	300 °C, 10 min, 3.9 wt%	300 °C, 5 min, 5 wt%	[65]
NiTiO ₃ nanoparticles	—	275 °C, 30 min, 6 wt%	150 °C, 60 min, 6 wt%	[66]
Nb ₂ C/Ni@MgH ₂ (MXene)	—	200 °C, 6 min, 6 wt%	200 °C, 6 min, 7 wt%	[29]

direct process-structure-property link. The incorporation route controls the near-surface availability of C@Ni adjacent to defect-rich (Ti/Nb)O_x domains, which in turn governs nucleation barriers, diffusion lengths, and the measured onset temperatures, activation energies, and low-temperature uptake.

Solar-driven platforms address the energy-input limitation of MgH₂ by integrating broad-band absorbers and catalytic constructs that deliver localized heating and facilitate H₂ activation and Mg-H bond scission. Representative studies report solar-driven reversible storage via Mg₂Ni(Cu) architectures and Cu@MXene photothermal layers. In parallel, light-enabled destabilization mechanisms in borohydrides leverage photogenerated vacancies to achieve hydrogen release and

uptake under mild conditions. Our catalyst design is orthogonal and complementary to these approaches. It uses only commercial powders and high-energy milling or mixing to generate defect-rich Ti/Nb sub-oxides and Ni-based sites, which already lower onset temperatures and activation energies under conventional thermal operation. Because these defect-rich oxides and Ni interfaces are compatible with photo-thermal scaffolds, future integration of our optimized MIX composites with light-harvesting layers could further reduce energy input while preserving the scalability of our processing route.

Beyond MXenes, several catalysts assembled from commercial oxides, salts, or carbons have demonstrated strong kinetics in MgH₂, including TiO₂ quantum dots [57], Nb₂O₅ hollow spheres [58], Ni or

NiO–niobate composites [77], and CeO₂@carbon systems [78]. These studies achieve rapid de/absorption under thermal operation, e.g., ~5.5 wt% at 300 °C in 5 min with Nb₂O₅ hollow spheres, or 5.5 wt% at 300 °C in 100 min for Co/CeO₂@C, but commonly require multi-step fabrication of tailored morphologies or heterostructures. In contrast, our catalyst is produced solely from commercial powders by ball milling or mixing, yet it lowers the dehydrogenation onset to ≤ 236 °C, reduces E_a by ≥ 44 kJ mol⁻¹, and enables low-temperature uptake down to 75 °C. We further note that high-performing MXene catalysts, although valuable benchmarks, rely on HF-based etching and remain non-commercial at scale, which complicates deployment relative to the present, milling-only route based on commodity oxides and KH.

5. Conclusions

Magnesium hydride (MgH₂) remains limited by slow sorption kinetics and elevated operating temperatures. Here, we demonstrate a scalable catalytic strategy based entirely on commercial powders employing a KH-modified TiO₂/Nb₂O₅ catalyst (CAT) combined with carbon-coated Ni nanoparticles (C@Ni)—incorporated into MgH₂ via ball milling (BM) or a two-step mixing route (MIX). This catalyst system consistently lowers the dehydrogenation onset temperature from 321 °C (as-milled MgH₂) to ≤ 236 °C and reduces the activation energy by ≥ 44 kJ mol⁻¹, to a minimum of 93.8 kJ mol⁻¹, depending on composition and processing route.

The optimized composites also deliver fast kinetics at 300 °C (~6.4–6.5 wt% H₂ desorbed in ~20 min) and meaningful performance at lower temperatures (e.g., ~2.7 wt% in 60 min at 260 °C). Notably, the MIX route enables exceptional low-temperature hydrogen uptake, with the MgH₂–1 wt% CAT–3 wt% C@Ni–MIX sample absorbing 5.77 wt% at 150 °C (50 min) and maintaining activity down to 100 °C (4.28 wt% in 120 min) and 75 °C (3.47 wt% in 120 min). Cycling tests show approximately 79% capacity retention after 20 cycles at 300 °C, indicating moderate durability with no evidence of contamination from ZrO₂ milling media.

Mechanistically, XPS and HRTEM reveal defect-rich reduced oxides (Ti³⁺/Nb⁴⁺) with abundant non-stoichiometric oxygen species, which, combined with Ni-assisted H₂ activation and spillover, rationalize the lower onset temperatures, reduced E_a, and enhanced low-temperature absorption.

Unlike many MgH₂ catalysts that rely on laboratory-specific or non-commercial materials, our methodology uses only commercial precursors and straightforward processing, yet achieves state-of-practice kinetic and thermal metrics. The combination of performance and scalability (together with the processing insight that the MIX route enhances low temperature uptake) positions this approach as a practical route toward deployable MgH₂-based hydrogen storage.

CRediT authorship contribution statement

Francisco J. Bolívar: Supervision, Project administration. **Carlos Arrieta:** Supervision, Project administration. **Félix Echeverría Echeverría:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Julian Arias Velandia:** Software, Resources, Formal analysis. **Robinson Aguirre Ocampo:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Alejandro A. Zuleta Gil:** Supervision, Project administration. **Julian A. Lenis:** Visualization, Data curation, Conceptualization. **Esteban Correa:** Writing – review & editing, Supervision, Project administration. **Sindy Bello:** Visualization, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2026.188174.

Data availability

Data will be made available on request

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