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Tailoring the hydrogen storage kinetics in MgH_2 by catalytic addition of K_2CrO_4

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Abstract-: Magnesium hydride (MgH_2) is regarded as one of the most promising solid-state hydrogen storage materials owing to its high hydrogen storage capacity, low cost, and excellent reversibility. However, its practical application is severely restricted by sluggish hydrogen sorption kinetics and high dehydrogenation temperature. In the present study, K_2CrO_4 was systematically investigated as a chromate-based catalyst to enhance the hydrogen storage performance of MgH_2. MgH_2+x wt.% K_2CrO_4 (x= 5,10,15) composites were synthesized via high-energy planetary ball milling, and their hydrogen storage behaviour was comprehensively evaluated using TG-DSC, Kissinger kinetic analysis, pressure-composition-temperature (PCT) measurements, XRD, SEM-EDX and XPS. Among the investigated compositions, the 10 wt.% K_2CrO_4 added composite exhibited the optimum catalytic performance, lowering the onset hydrogen desorption temperature by approximately 100 ºC compared with pristine MgH_2. Kissinger analysis revealed a reduction in activation energy to 130.7 ± 4.1 kJ/mol for the catalysed composite, confirming a significant improvement in dehydrogenation kinetics. PCT measurements demonstrated that K_2CrO_4 primarily enhances the reaction kinetics without significantly affecting the thermodynamic properties of MgH_2. XRD analysis confirmed the reversible phase transformation between MgH_2 and Mg, while SEM-EDS revealed a homogeneous catalyst distribution throughout the hydride matrix. XPS investigations further indicated that partial reduction of surface Cr(VI) species during ball milling and thermal treatment generated catalytically active mixed-valence chromium sites, which facilitate interfacial charge transfer and weaken the Mg-H bond. These findings establish K_2CrO_4 as an effective chromate catalyst and provide new mechanistic insights into the catalytic enhancement of MgH_2 for solid-state hydrogen storage applications.

Keywords:- Hydrogen Storage, Magnesium Hydride (MgH_2), K_2CrO_4, Catalyst, Sorption Kinetics.

1. INTRODUCTION

In this modern era energy is basic and important need of humankind to improve the civilization and industrialisation process. This demand is rapidly accelerating with the time across the world and in the present scenario the conventional energy sources are unable to fulfil the demand [1]. Also, some facts such as the nature of carbon emission, limited quantity, low gravimetric energy density, geographical availability are obstacles in their long-term use as energy sources [2,3]. Seeing the above-mentioned issues the renewable energy sources are alternative solutions to replace the conventional energy systems and hydrogen energy have very promising behaviour in that. Hydrogen is very green and clean source of energy, have very high gravimetric energy density (LHV is 120 MJ/kg) which is almost 3 times higher than conventional carbon-based fuel such as gasoline [4]. However, the safer and easy storage remains one of the major bottlenecks limiting its large-scale practical application [5]. Solid state storage of hydrogen in the form of metal hydride is a feasible approach for safer storage and specially MgH_2 emerged as suitable candidate due to its theoretical specific capacity of 7.6 wt.% of storing hydrogen which exceeds the US-DOE goals [6,7] . However, MgH_2 suffer from slow kinetics and high thermodynamic stability due to strong Mg-H bonding that leads it to high temperature operation (~ 400 ºC) for hydrogen desorption [8].

Several strategies have been explored to overcome the intrinsic limitations of MgH_2, including nano-structuring, alloying, catalyst incorporation, and mechanical activation [8–11].

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Among these, catalyst addition has emerged as one of the most effective approaches because it significantly enhances the hydrogen sorption kinetics while largely preserving the high theoretical hydrogen storage capacity of MgH_2. A wide variety of catalysts, including transition metals, metal oxides, ternary metal oxides, halides and carbon-based materials, have been investigated to reduce the hydrogen desorption temperature and activation energy [10–15]. Furthermore, the combination of catalyst incorporation with high-energy ball milling has proven particularly effective in producing refined microstructures, increasing lattice defects, and promoting intimate catalyst-hydride contact, thereby facilitating hydrogen diffusion and accelerating the dehydrogenation kinetics of MgH_2 [16].

Among the investigated catalyst systems, ternary transition metal oxides have received considerable attention owing to their multiple accessible oxidation states and ability to participate in reversible surface redox reactions during hydrogen sorption [17]. Such characteristics facilitate interfacial charge transfer, weaken the Mg-H bond, and improve the dehydrogenation and rehydrogenation kinetics of MgH_2. Consequently, numerous transition metal oxides, including TiO_2, Nb_2O_5, V_2O5, Fe_2O_3, Cr_2O_3, $KNbO_3$, $Li_4Ti_5O_{12}$, and Na_2CrO_4, have been successfully employed as catalysts for MgH_2 [18–25]. These studies indicate that the catalytic performance strongly depends on the catalyst composition, electronic structure, and the nature of the catalyst-hydride interface.

In particular, chromium-based compounds have recently attracted growing interest because of their favourable redox behaviour and catalytic stability. In our previous study, Na_2CrO_4 was demonstrated to be an effective catalyst for MgH_2, leading to a substantial reduction in the activation energy and enhanced hydrogen desorption kinetics [25]. The catalytic behaviour of chromate compounds is believed to arise from the synergistic contribution of the alkali metal cation and chromium oxyanion. While the alkali metal promotes effective catalyst dispersion during ball milling and facilitates hydrogen diffusion through defect generation, chromium species provide catalytically active redox centres that weaken the Mg-H bond via interfacial charge transfer. Such synergistic interactions suggest that replacing Na^+ with K^+, which possesses a larger ionic radius and different electronic characteristics, may modify the catalyst-hydride interface and consequently influence the hydrogen sorption behaviour of MgH_2.

Despite the encouraging performance of chromium-based catalysts, the catalytic effect of K_2CrO_4 on the hydrogen storage properties of MgH_2 has not been systematically investigated. Therefore, the present work aims to explore the influence of K_2CrO_4 addition on the dehydrogenation behaviour, activation energy, thermodynamic characteristics, phase evolution, morphology, and surface chemical states of MgH_2. These promising results of Cr based additives are key motivators for the incorporation of Cr based ternary metal oxide K_2CrO_4 in MgH_2 and this study is representing the study of composites synthesised in various ratios and the catalytic mechanism has been elucidated through a combination of thermal, structural, microscopic, and X-ray photoelectron spectroscopy analyses, providing further insights into the role of chromate-based catalysts in magnesium hydride systems.

2. EXPERIMENTAL

Sample Synthesis

All the precursors MgH_2 and K_2CrO_4 of 99.9 % purity were purchased from Sigma-Aldrich. MgH_2 and K_2CrO_4 were ball milled using Fristch P7 ball milling machine. The ball milling was done in the SS milling pot of 30 cm^3 and 20 SS balls of 7 mm diameter were used for milling of 1gram composite when the rotation speed was kept 400 rpm for a total of 2 hours in the 1-hour milling and 30 minutes rest pattern. The composites were prepared in the ration of MgH_2+5 wt.% K_2CrO_4, MgH_2+10 wt.% K_2CrO_4, MgH_2+15 wt.% K_2CrO_4 and pristine MgH_2 as reference sample. All the sample preparation and milling were done in 0.1 MPa Ar atmosphere in a glove box Miwa MFG, MP-P60W where oxygen and moisture levels were maintained below 1 ppm.

A thermogravimetric analysis machine (Rigaku TG 812) was used to test the hydrogen mass desorption properties of the samples in the temperature range from toom temperature to 400 ºC at the heating rate of 5 ºC/min. This study was carried out in the Ar environment of 0.1 MPa pressure. While the Differential Scanning Calorimetry (TA Instruments, Q 10 PDSC) was used to obtain desorption events during heat treatment up to 450 ºC of the sample in presence of Ar. Heat treatments were done on heating rates of 1, 2, 5, 10 ºC/min.

X-Ray Diffraction of the sample after every experiment was performed on RIGAKU RINT-2000 machine having source of Cu K_α, wavelength of 1.54 Å to carry out structural and phase information in the sample during across the experimental treatments. XRD was performed in the 2-theta range of 10-80º where 2 º/min was the scanning rate. Sample preparation was done in inert atmosphere glove box and further to isolate the samples from the atmospheric environment during the sample transfer for XRD they were covered with the polyamide sheet with the help of vacuum grease. The similar strategy was used for the sample transfer for SEM-EDX where HITACHI, S-4800, was equipped for the morphological and elemental analysis of the samples in as milled and heat-treated

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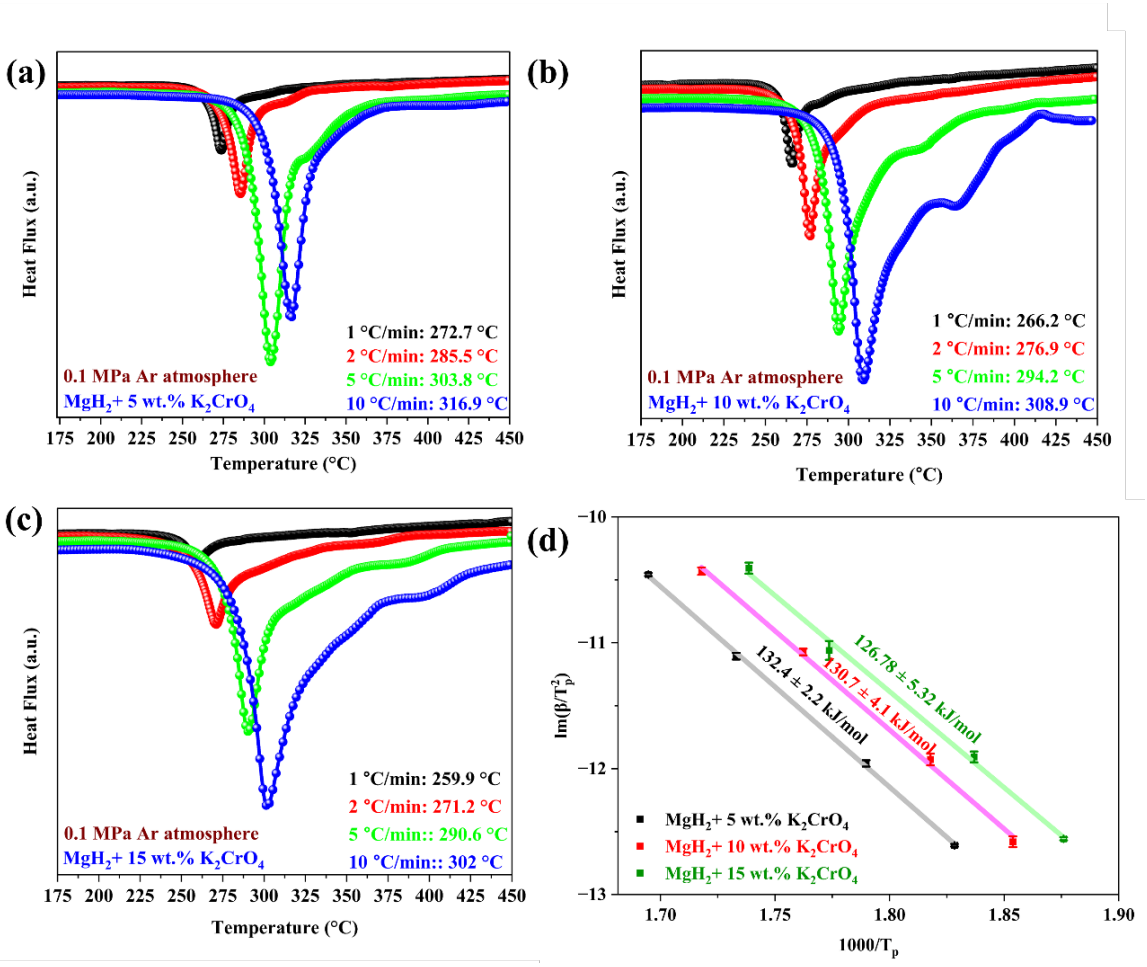
states. To explore the surficial catalytic activity the survey and narrow scans of XPS were performed for all the elements present in the samples in their as milled and heated conditions using the Thermo-Fisher Scientific ESCALAB 250Xi XPS machine with an X-ray source of Al-K$_\alpha$ (1486.6 eV). A special arrangement of vacuum based chamber was used for sample transfer for XPS test.

3. RESULTS AND DISCUSSION

De/Hydrogenation Study

Differential Scanning calorimetry (DSC)

To evaluate the hydrogen desorption behaviour of prepared composites the differential scanning calorimetry (DSC) test was performed for all the samples. For the evaluation, all as-milled samples were utilised, and test was run on all four heating rates in pure Argon environment. the calorimetric behaviour of the samples is shown in the Figure 1. The composites MgH_2 + 5 wt.% K_2CrO_4, 10 wt.% K_2CrO_4 and 15 wt.% K_2CrO_4 shown hydrogen desorption at temperatures 303.8, 294.2 and 290.6 ºC respectively at heating rate of 5 ºC/min. It is worth to be noted that increment in the concentration of catalyst amount resulted in lowering the desorption temperature. In our previous study pristine MgH_2 desorbed hydrogen at 417 ºC at 5 ºC/min heating rate (Reference) thus conclusively it can be said that addition of K_2CrO_4 lowered the desorption temperature by ~100 ºC in the MgH_2. To comprehensively analyse the catalyst effect, activation energy of the sample was also calculated using all peak desorption temperature (at heating rates of 1, 2, 5, 10 ºC/min) as shown in Table 1. Non-isothermal method of calculating activation energy using the Kissinger equation was utilised in the study. The Kissinger equation is as follows:



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$$ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + ln\left(\frac{AR}{E_a}\right) \qquad \ldots (1)$$

Figure 1: DSC Curves for (i) MgH_2 + 5 wt.% K_2CrO_4 (ii) MgH_2 + 10 wt.% K_2CrO_4 (iii) MgH_2 + 15 wt.% K_2CrO_4 (iv) Kissinger plot for activation energy (E_a).

Table 1: Peak desorption temperature (T_p) for DSC in 0.1 MPa Ar Atmosphere at various heating rates

Peak Temperature (T_p) on Heating Rate / **Sample**	**1 ºC/min**	**2 ºC/min**	**5 ºC/min**	**10 ºC/min**
MgH_2 + 5 wt.% K_2CrO_4	272.7 ºC	285.5 ºC	303.8 ºC	316.9 ºC
MgH_2 + 10 wt.% K_2CrO_4	266.2 ºC	276.9 ºC	294.2 ºC	308.9 ºC
MgH_2 + 15 wt.% K_2CrO_4	259.9 ºC	271.2 ºC	290.6 ºC	302 ºC

In this equation, β represents the heating rate, (T_p) denotes the peak temperature at different heating rates, (E_a) is the activation energy, (R) is the universal gas constant (8.314 J mol^{-1} K^{-1}), and (A) corresponds to the pre-exponential (frequency) factor. Obtained peak temperature were used to calculate the activation energy in the composites. Here the MgH_2 catalysed with 5 wt.% K_2CrO_4 shown activation energy 132.4 ± 2.2 kJ/mol, with 10 wt.% it was 130.7 ± 5.3 kJ/mol and for addition of 15 wt.% K_2CrO_4 it was 126.7 ± 4.1 kJ/mol. These activation energies of desorption are lower than the pristine MgH_2 which shows impactful effect of K_2CrO_4 in improving desorption kinetics.

Thermogravimetric Analysis (TGA)

To evalutate the amount of hydrogen which is released by composites the thermogravimetruic analysis was performed for all the samples in the presence of Ar gas at pressure of 0.1 MPa. The thermal treatment provided to the sampe was fom room temperature to 400 ºC and the mass loss was recorded during all oer the procedure. The compite MgH_2+ 5 wt.% started to desorb hydrogen at 256 ºC and upto the 400 ºC the total released amount was 7.2 wt.%. In the 10 and 15 wt.% K_2CrO_4 added MgH_2 the hydrogen desorption is 6.8 wt.% and 6.2 wt.% respectively while the onset temperature was lower as 221.7 & 212.4 ºC respectively. The overall hydrogen release in all the composites are very close to their theoritical values (including the mass of catalyst). However among all, the 10 wt.% catalyst K_2CrO_4 added MgH_2 shown balanced performance in terms of activation energy which ia comparabe in all three composites and in terms of hydrogen release amount it is superior dur to low dead mass comtributioin of catalyst. The observed hydrogen desorption behaviour indicates that K_2CrO_4 effectively enhances the dehydrogenation kinetics of MgH_2 while maintaining its intrinsic hydrogen storage capability. Although increasing the catalyst content provides additional catalytic interfaces, it also introduces a larger proportion of inactive mass, resulting in a gradual reduction in the gravimetric hydrogen capacity. Therefore, an optimum catalyst concentration is essential to achieve a balanced combination of enhanced kinetics and high hydrogen storage performance. Thus this concentratiuon of the sample was denoted as optimised one and several other tests were perfoemed on it for the deeper understaing of the system.

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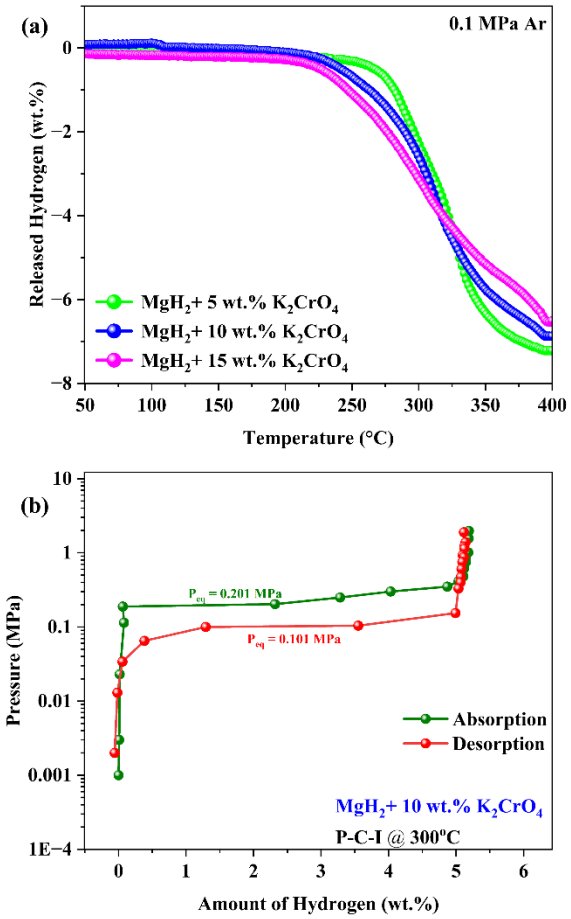

Figure 2: (a) Thermogravimetric analysis of as prepared MgH_2+ x wt.% K_2CrO_4 (x= 5, 10, 15) samples (b) PCI at 300 ^oC.

Pressure-Composition-Temperature (PCT) Isotherms

The optimized sample having 10 wt.% concentration of K_2CrO_4 was further examined by sievert type apparatus to obtain pressure composition isotherms for both hydrogen absorption and desorption. Both Hydrogen uptake and the release in the composites corresponded to single plateau in each reaction and the absorption equilibrium pressure (P_{abs}) was 0.201 MPa while desorption equilibrium pressure (P_{des}) 0.101 MPa. Thus, this isothermal volumetric measurement found to be consistent with pristine MgH_2 which usually elucidate single plateau. The PCT measurements further confirm that the incorporation of K_2CrO_4 does not significantly alter the thermodynamic stability of the MgH_2 system, as evidenced by the negligible change in the equilibrium plateau pressure. Instead, the catalyst primarily influences the reaction kinetics by facilitating hydrogen desorption without modifying the intrinsic hydride equilibrium. This observation is consistent with the DSC and activation energy analyses, indicating that K_2CrO_4 acts predominantly as a kinetic catalyst while preserving the reversible hydrogen storage characteristics of MgH_2.

Structural, Morphological and Chemical Analysis

X-Ray Diffraction (XRD)

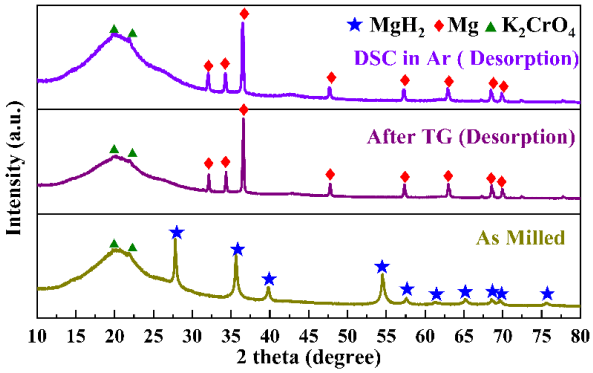

Figure 3: X-ray diffraction patterns of MgH_2 + 10 wt.% K_2CrO_4 in the as-milled state and after thermal treatments by DSC and TG experiments.

X-ray diffraction of the optimized sample was carried out at several experimental procedures like in as milled state, after TG and DSC and picturised in the Figure 3. In this crystallographic test as-milled sample was carrying the peaks corresponding to the MgH_2 and K_2CrO_4 phases aligned with the standard database having JCPDS No. 00-012-0697 and 00-015-0359 respectively. Major peaks corresponding to MgH_2 were at the positions of 27.8, 35.6, 39,7 & 54.7º while very minor intensity peaks of K_2CrO_4 due to its low content in the sample with respect to MgH_2 were observed at 19.9 & 21.9º. When the sample was treated in the TG & DSC experiments for the desorption ex-situ XRD was performed and as observed in the Figure 3 no traces were observed for the MgH_2 phase resulted the formation of Mg metallic phase.

This Mg phase is correlated to the JCPDS No. 00-035-0821 while peaks corresponding to the K_2CrO_4 remained at same position with the same intensity. This complete conversion of phases during experiments validates the complete dehydrogenation in the given temperature range while no extra peaks observation implies that K_2CrO_4 remained stable in the sample without altering the reaction path of Mg/MgH_2.

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Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

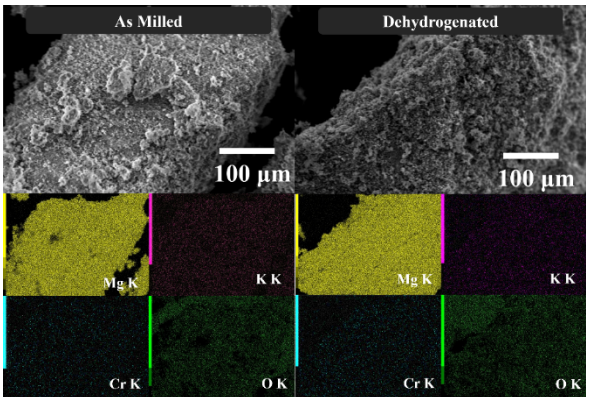

Figure 4: SEM-EDX of As-milled and dehydrogenated sample.

To surmount the morphological changes and observe any effect on the elemental distribution of the catalyst in the sample SEM along with EDX analysis was performed of as milled and dehydrogenated (heated in dynamic vacuum at 400 ºC) samples shown in Figure 4. The as milled sample shown all the elements are present uniformly which validates sufficiency of 2 hours milling for proper incorporation of the catalyst in the matrix of MgH_2. Micrometre range particles are seen in the SEM image after milling. After heating no change in the morphology and particle size is seen in the sample while the catalytic elements also remained intactly well distributed. The uniform dispersion of K_2CrO_4 together with the reduced particle size is expected to promote efficient catalyst-hydride contact, thereby facilitating hydrogen diffusion and enhancing the dehydrogenation kinetics of MgH_2. These morphological observations are in good agreement with the improved thermal behaviour revealed by DSC and TG analyses.

X-ray Photoelectron Spectroscopy (XPS)

To probe the surficial study of optimized samples and the behaviors of the catalytic elements in the sample XPS study of the As Milled and Heated sample of MgH_2 + 10 wt.% K_2CrO_4 was done as well as the Pure K_2CrO_4 was tested under the identical condition for the referencing. Initially a broad survey was conducted for all the elements and further narrow scans for them were done. All the deconvolutions were made using the CasaXPS software keeping adventitious carbon C 1s as reference at binding energy of 284.8 eV and shown in Figure 5. Both catalytic elements K and Cr of K_2CrO_4 were analyzed for 2p spectra which split into $2p_{3/2}$ and $2p_{1/2}$ due to spin-orbit coupling. K 2p spectra of pure K_2CrO_4 is very well fitted by single-single peaks situated at 292.7 eV for K $2p_{3/2}$ and 295.76 eV for K $2p_{1/2}$. These peak positions are confined to the K^+ oxidation state in K_2CrO_4 compound according to the previous literature [26]. While it was ball milled with MgH_2 and further heated, the signal intensities were very low due to smaller fraction of it in the sample. Small deviation in the binding energy values was found as modifications in the local electronic environment occurred during interaction with the MgH_2 matrix, but the signals were corresponding to existence of compound K_2CrO_4 and well matched with the XRD analysis.

On the other hand, the Cr 2p spectra of pure K_2CrO_4 sample is also fitted with single pair of doublets positioned at 579.71 eV & 588.64 eV which correspond to the oxidation state of Cr(VI) in K_2CrO_4 compound and supports interpretation from the K 2p spectra of pure catalyst [27]. Interestingly, when the K_2CrO_4 was milled with MgH_2 the spectra got broadened, less intense and shifted towards lower binding energy side and could be fitted with two doublets of representative peaks at 575.06/584.6 eV & 579.05/588.78 eV. In the spectra it is visible that along with the peaks of higher binding energy have been suppressed in the intensity by the emergence of additional peaks at lower binding energy. The reduction of a fraction of surface Cr(VI) species suggests that K_2CrO_4 actively participates in the dehydrogenation process through surface redox interactions rather than behaving as an inert additive and partially reduced to the lower oxidation states of Cr as suggested in the previous studies [28]. During the high-energy ball milling, repeated fracture and cold welding of MgH_2 particles generate fresh reactive surfaces, lattice defects, and localized high-energy regions, which facilitate electron transfer from the hydride matrix to these chromium species [29]. Consequently, partial reduction of Cr(VI) occurs, giving rise to lower oxidation-state chromium species that remain highly dispersed on the particle surface. Since no additional crystalline chromium-containing phases were detected by XRD, these species are likely amorphous or nano dispersed and therefore remain below the detection limit of XRD.

The coexistence of Cr(VI) and reduced chromium species indicates that K_2CrO_4 undergoes only partial surface transformation during mechanochemical processing and subsequent thermal treatment. Such mixed-valence chromium sites can modify the local electronic environment at the catalyst-hydride interface, facilitating charge transfer during hydrogen desorption. The generation of these catalytically active surface species is expected to weaken the interfacial Mg-H interactions and promote hydrogen diffusion from the bulk

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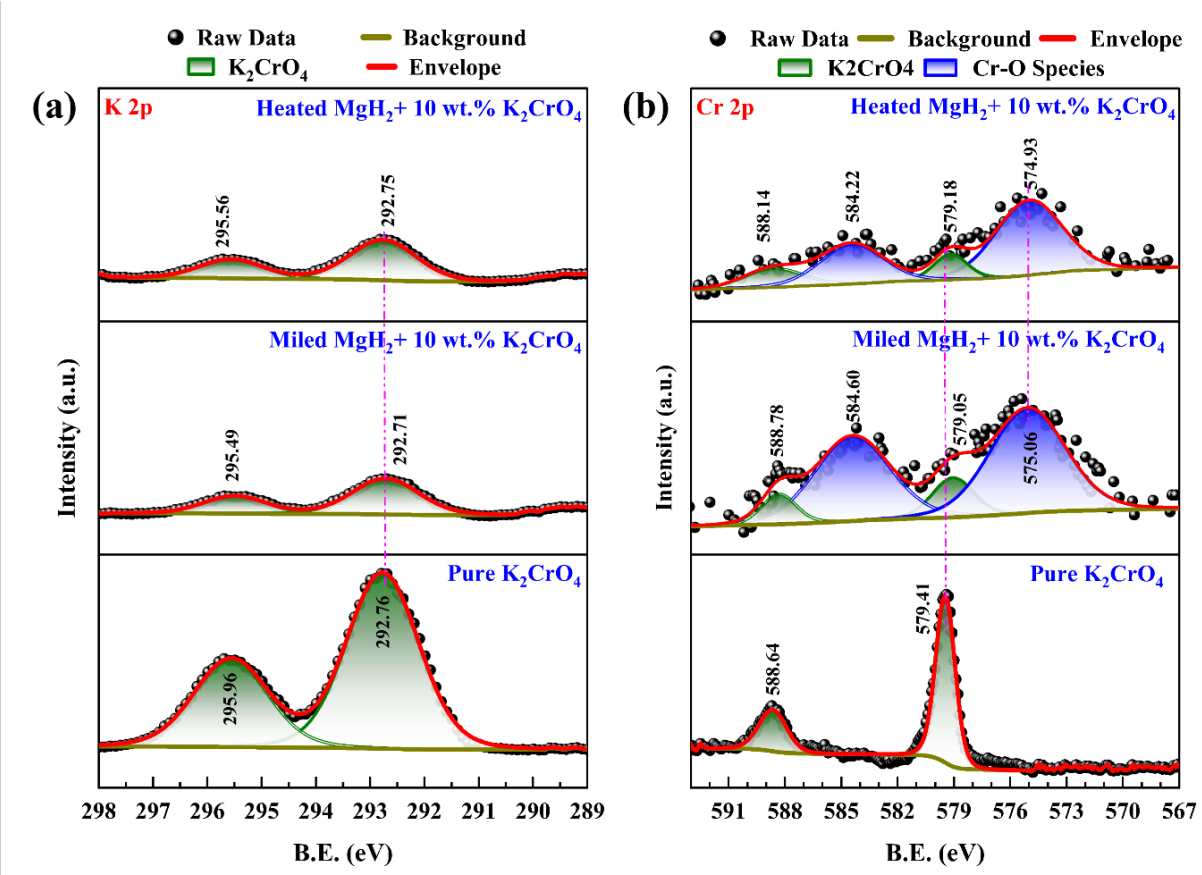
toward the particle surface, thereby contributing to the observed reduction in the hydrogen desorption temperature and activation energy.

Figure 5: X-ray photoelectron spectroscopy of MgH_2 + 10 wt.% K_2CrO_4 sample for the elements (a) K 2p (b) Cr 2p



Overall, the XPS investigation demonstrates that the catalytic behaviour of K_2CrO_4 is primarily associated with the surface evolution of chromium species during milling and dehydrogenation. Although the bulk crystal structure of K_2CrO_4 remains preserved, as confirmed by XRD, the formation of highly dispersed reduced chromium species at the surface provides direct evidence that the catalyst participates in the reaction through surface electronic interactions, thereby enhancing the dehydrogenation kinetics of MgH2.

The combined results obtained from DSC, TG, PCT, XRD, SEM-EDX, and XPS consistently demonstrate that K_2CrO_4 enhances the hydrogen desorption behaviour of MgH_2 primarily through a surface-mediated catalytic mechanism. Thermal analyses confirm improved dehydrogenation kinetics, whereas structural characterization reveals that the catalyst remains crystallographically stable. XPS further demonstrates partial surface reduction of chromium species, indicating that the catalytic activity originates from interfacial electronic interactions rather than bulk phase transformation.

4. CONCLUSION

In this work, the catalytic influence of K_2CrO_4 on the hydrogen storage behaviour of MgH_2 was systematically investigated through thermal, structural, morphological, and surface chemical analyses. High-energy ball milling successfully produced homogeneous MgH_2- K_2CrO_4 composites, and among the investigated compositions, the 10 wt.% K_2CrO_4 sample exhibited the most balanced hydrogen storage performance. The incorporation of K_2CrO_4 reduced the hydrogen desorption

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temperature of MgH_2 by approximately 100 ºC compared with pristine MgH_2, while the activation energy decreased from about 169.9 kJ/mol to 130.7 kJ/mol, confirming a substantial enhancement in the dehydrogenation kinetics. Thermogravimetric analysis further demonstrated that the optimized composite maintained a hydrogen storage capacity close to its theoretical value, whereas PCT measurements confirmed that the catalyst did not alter the intrinsic thermodynamic equilibrium of the MgH2 system, indicating that K_2CrO_4 functions primarily as a kinetic catalyst.

The structural evolution investigated by XRD revealed the complete transformation of MgH_2 into metallic Mg during dehydrogenation, while the K_2CrO_4 phase remained crystallographically stable without generating detectable secondary crystalline products. SEM-EDX analysis further confirmed the uniform distribution of the catalyst throughout the MgH_2 matrix after ball milling and thermal treatment, ensuring effective catalyst-hydride contact. More importantly, XPS investigation provided direct evidence that although the bulk K_2CrO_4 phase remained preserved, a fraction of surface Cr(VI) species underwent partial reduction to lower oxidation states during mechanochemical processing and subsequent heating. The coexistence of mixed-valence chromium species suggests the formation of catalytically active interfacial sites that facilitate charge transfer, weaken the Mg-H interaction, and promote hydrogen diffusion, thereby accelerating the dehydrogenation reaction.

Overall, this study demonstrates that K_2CrO_4 is an effective chromium-based kinetic catalyst for MgH_2 and establishes that its catalytic activity originates predominantly from surface electronic interactions rather than bulk phase transformation. These findings provide new insights into the catalytic mechanism of chromate additives and offer a promising strategy for the rational design of alkali metal-transition metal oxide catalysts for advanced solid-state hydrogen storage applications.

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