

Decoding the anomalies on the in-situ generated catalytic species in ceria catalyzed hydrogen storage system MgH₂ by Raman spectroscopy

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Owing to the high gravimetric hydrogen density (7.6 wt.% H₂) and appreciable reversibility (>95%), magnesium hydride (MgH₂) is considered as the most suitable hydrogen storage material for vehicular applications (target capacity for hydrogen vehicles: 5.5 wt.% H₂)¹. Nonetheless, the high operating temperature (>350 °C) remains a potential drawback with the commercial MgH₂ samples. On the other hand, it is presently clear that this operating temperature can be lowered by at least 50 °C through the incorporation of ceria (CeO₂) as additive for MgH₂. Studies reported in the literature² suggest that MgH₂ and the additive CeO₂ interact chemically and produces a product CeH₂ and this in-situ generated product is the actual catalyst responsible for destabilizing MgH₂. In contrast to this, the detailed study performed by the current team³ suggest that in the earlier studies the reduced cerium oxide phase(s) may be mistaken as cerium hydride(s) and hence the following conclusion, “CeH₂ as the active in situ catalyst in MgH₂/CeO₂ hydrogen storage system”, may not be accurate. To clarify these, we have prepared two different nanocomposite powders, MgH₂+0.167CeO₂ and MgH₂+0.5CeO₂ by mechanical milling (5 h/200 rpm) technique. The tests conducted at various stages of hydrogenation/dehydrogenation cycles (cycles: 1, 5 and 10) revealed that mild chemical interaction between MgH₂ and CeO₂ occurs at the time of mechanical milling, whereas strong redox type interaction occurs after recycling the power under hydrogen ambience. Interestingly, although the high temperature in-situ XRD technique prove that thermally activated interaction between MgH₂ and CeO₂ does not result to the formation of MgO, no convincing conclusions can be made regarding the existence or absence of the other phase CeH₂. On the other hand, the in-situ / ex-situ Raman spectroscopy provides crucial evidence that reduced cerium oxides in higher quantities exist at all stages of interactions in the MgH₂/CeO₂ hydrogen storage system. Further advanced electron microscopic observations concur well with the observations made by Raman spectroscopy. This clarification regarding the actual catalytic species in ceria catalyzed MgH₂ is a breakthrough development because it potentially assists us to formulate the catalytic mechanism of this hydrogen storage system. This is interesting to note that, in certain circumstances, (as for example, the current ceria catalyzed MgH₂ system), when powerful tools like XRD remains inconclusive, Raman spectroscopy provides the accurate picture regarding the underlying chemical phenomena.

Acknowledgement: This work was supported by CENTRO-01-0145-FEDER-022083 – Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). D.P acknowledges the funding through the ECIU-SMART-ER SEED research project, year 2022-2023.

References

- [1] D. Pukazhselvan et al. Nano Energy 1(4):566-589 (2012).
- [2] Mustafa et al, J. Alloys Compd., 695:2532-2538 (2017).
- [3] D. Pukazhselvan et al. Appl. Surf. Sci. 561:150062 (2021).