Exploring the impact of doping on the cyclic stability in the steam-iron process

Carola Kuhn[1], Anna Knapp[1], Steffen Tischer[2], Olaf Deutschmann*[1,2]

1 Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstraße 20, 76131 Karlsruhe, Germany
2 Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
**Corresponding author: deutschmann@kit.edu*

Highlights

- Synthesis method decisively impacts system performance.
- Optimal performance is achieved with 5 mol% additive loading.
- Adding molybdenum led to enhanced stability over 50 cycles.

1. Introduction

Hydrogen is a carbon-free energy carrier that has great potential for widespread use, but requires appropriate infrastructure and storage concepts. One approach that has been widely discussed is the indirect storage of hydrogen in metal oxides, with a particular focus on the Fe_xO_y/Fe system [1]. This involves the cyclic process of storing and recovering hydrogen via reduction of iron oxides and oxidation of iron with water vapor (steam-iron process). The primary challenge of the steam-iron process is the diminishing activity with an increasing number of cycles. However, it has been demonstrated that the inclusion of structural promoters, such as aluminum, molybdenum, and cerium, substantially enhances cyclability [2]. To gain a more detailed understanding, a comprehensive parameter study was conducted to analyze the effects of these three additives on the steam-iron process. This research investigated the influence of the additive loading and synthesis approach on the performance of hydrogen production, in addition to examining the particular influence of the additive.

2. Methods

The modified iron oxides were synthesized using co-precipitation (Al, Ce) and impregnation of Fe_2O_3 (Al, Ce, Mo). Additive concentrations of 2, 5 and 10 mol% were analyzed. The performance of the various modified oxides was investigated in a fixed-bed reactor operating at 600 °C with a flow rate of 300 mL/min (Red: 5 % H_2, Ox: 20 % H_2O balanced with N_2).

3. Results and discussion

Comparison of synthesis methods indicates that impregnation produces significantly better stability results than co-precipitation. This is due to the higher proportion of additive on the particle surface achieved through impregnation, which helps prevent sintering effects. The optimal loading of additives investigated is 5 mol%. A higher loading leads to a significant reduction in the hydrogen storage capacity because of the formation of mixed oxides, such as $FeAl_2O_4$, which no longer actively participate in the redox process. Figure 1 shows the hydrogen production of the doped samples over 16 cycles compared to pure Fe_2O_3. The results indicate a significant improvement in performance with the addition of a dopant. Initially, hydrogen production remains stable for all additives. However, the Ce-doped sample shows a marked decrease in activity from the 8th cycle onwards. The Al-doped sample experiences a slight decrease in activity after the 8th cycle, whereas the Mo-doped sample maintains constant activity. SEM images of the samples after cyclization reveal that the incorporation of Al and Mo is more effective in preventing particle sintering compared to the addition of Ce, resulting in higher activity. A long-term experiment lasting 50 cycles at 600°C with 5 mol% Mo was conducted, which resulted in a gradual decrease in hydrogen production to 10 mmol·g^{-1}. Despite this decline, the performance of the experiment was still significantly better than that of pure Fe_2O_3, where hydrogen production drops to 6 mmol·g^{-1} after only 5 cycles.

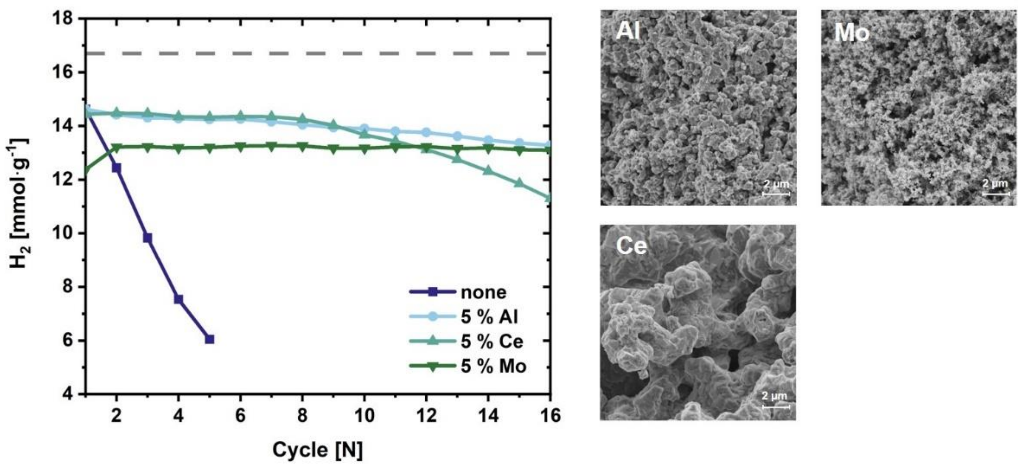

Figure 1: Hydrogen production of the impregnated samples per cycle in comparison to pure Fe_2O_3 and SEM images of the respective samples after 16 cycles. The dotted line represents the theoretical storage capacity of pure Fe_2O_3.

4. Conclusions

The steam-iron process emerges as a promising approach for the cyclical indirect storage and release of hydrogen. The introduction of Al, Mo, and Ce additives has proven effective in significantly mitigating deactivation, with Mo standing out as the most promising candidate, demonstrating robust performance over 50 cycles under the examined conditions.

References

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