

Effect of sodium carbonate substitution and addition of inorganic particles on the sodium manganese ferrite thermochemical cycle (O-2H-V)

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1. Introduction

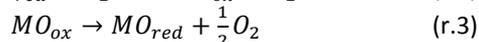
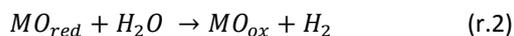
Hydrogen will play a crucial role in the energy transition due to its high potential to contribute to the decarbonization of the economy. Green hydrogen, produced from energy from renewable sources or residual waste heat, will serve as raw material for the chemical industry, particularly in carbon dioxide-emitting industrial sectors (steel plants, refineries, cement plants), for mobility, for the residential and tertiary sectors, and for massive energy transportation or long-time energy storage. This last point is especially important since energy generation, in the case of renewables, does not always match in time with its demand.

Green hydrogen can be produced from water by electrolysis or direct thermal decomposition according to Reaction 1.



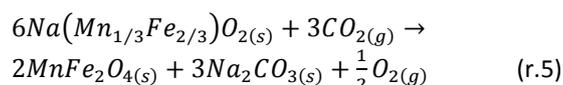
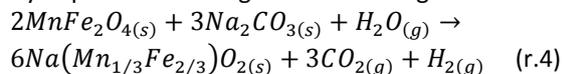
One of the main drawbacks of direct thermal decomposition is that the reaction only proceeds for temperatures above 2800 K. However, water thermal decomposition can be performed at significantly lower temperatures, i.e. 973 – 1273 K, through a multi-step approach using thermochemical cycles [1]. Thermochemical cycles are composed by multi-step processes that form a closed cycle, in which the overall reaction is Reaction 1.

A generic two-step process makes use of metal oxides as a redox pair, MO_{ox}/MO_{red} according to the following reactions:



This way, the intermediate reactants can be recycled whereas hydrogen and oxygen are released in different steps [2].

Among two-step thermochemical cycles for water splitting, the one proposed by Tamaura [3] exhibits a considerably low operation temperature, i.e. 973 – 1073 K [4]. This cycle is generally depicted according to the following reactions:



However, the production of hydrogen decreases upon cycling, compromising the industrial implementation of the process [4].

In this work, two strategies have been tested in order to improve the cyclability of the process: the substitution of pure Na₂CO₃ by mixtures of alkali metal carbonates and the addition of inorganic particles to the reaction mixture.

2. Experimental

2.1 Material and methods

First, pure Na₂CO₃ was substituted by three different alkali metal carbonate mixtures: a) a Li₂CO₃:Na₂CO₃ mixture with a molar ratio of 0.07:0.93 namely 0.07LiNa, b) a Li₂CO₃:Na₂CO₃ mixture with a molar ratio of 0.5:0.5 namely 0.5LiNa, and c) a Li₂CO₃:Na₂CO₃:K₂CO₃ mixture with a molar ratio of 0.32:0.33:0.35 namely LiNaK. The stoichiometric MnFe₂O₄:Na₂CO₃ molar ratio of the original cycle, i.e. with pure Na₂CO₃, is 2:3. Consequently, the MnFe₂O₄:Carbonate mixture mixtures were prepared using this molar ratio. The results were compared with the ones obtained using the original MnFe₂O₄:Na₂CO₃ mixture, namely Na.

Secondly, the addition of SiO₂ and CeO₂ in the original MnFe₂O₄:Na₂CO₃ cycle was evaluated. The SiO₂ and CeO₂ were first mixed in a mortar with the MnFe₂O₄ spinel. The obtained mixtures were then mixed with pure Na₂CO₃ to achieve a MnFe₂O₄:Na₂CO₃ molar ratio of 2:3. These resulting mixtures were named as Si-Na and Ce-Na.

The cyclability of the prepared mixtures was studied in a STA 449 Jupiter thermobalance (Netzsch). The mixtures were submitted to five consecutive thermochemical cycles consisting of two reaction steps: the decarbonation step (Reaction 4) and the carbonation step (Reaction 5). Before the first cycle, the reaction mixture was heated up to 750 °C under 100 mL/min of N₂ with a heating ramp of 10 °C/min. Later, in the decarbonation step, the mixture reacted at 750 °C in the presence 100 mL/min of N₂ and 0.5 g/h of water vapor. The carbonation reaction was carried out at the same temperature in presence of 100 mL/min of CO₂. Each thermochemical cycle lasts approximately 24 h. For the first cycle, the duration of the decarbonation step was 5 h, while 3 h were used for the successive cycles. The produc-

tion of hydrogen during the decarbonation step was measured using a Unisense H₂ UniAmp sensor. All the mixtures, before and after the cyclability tests, were characterized by XRD and SEM.

3. Results and discussion

3.1 Cyclability test

The hydrogen productions upon cycling for all the studied mixtures are shown in Table 1.

Table 1. Hydrogen production per cycle for the studied mixtures

Mixture	Hydrogen production (mmol H ₂ /g _{mixture})					
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Total
Na	1.10	0.05	0.04	0.03	0.01	1.24
0.07LiNa	0.87	0.05	0.02	0.00	0.00	0.94
0.5LiNa	0.41	0.00	0.00	0.00	0.00	0.41
LiNaK	0.10	0.00	0.00	0.00	0.00	0.10
Si-Na	0.37	0.00	N.D.	N.D.	N.D.	N.D.
Ce-Na	0.67	0.06	0.05	0.05	0.06	0.88

N.D.= Non-data.

As reported in the literature [4], the results indicate that the original cycle has a low cyclability at the used operating conditions. After the first cycle, the hydrogen production decreases significantly from 1.10 mmol H₂/g_{mixture} to 0.05 mmol H₂/g_{mixture}. On the following cycles, the hydrogen production continues to decrease reaching a value of 0.01 mmol H₂/g_{mixture} for the fifth cycle.

Regarding the carbonate substitution, i.e. 0.07LiNa, 0.5 LiNa and LiNaK mixtures, the results suggest that substituting Na₂CO₃ by other carbonate mixtures did not improve the cyclability of the process in terms of hydrogen production. The best result was obtained for the 0.07LiNa mixture with a hydrogen production of 0.87 mmol H₂/g_{mixture} for the first step. However, this mixture exhibits a similar behaviour as the Na mixture. The hydrogen production decreases significantly after the first cycle reaching a value of 0.00 mmol H₂/g_{mixture} for the fourth cycle. However, the 0.07LiNa mixture exhibits a faster reaction kinetics and a higher cyclability in terms of mass variation. The 0.5LiNa and the LiNaK mixtures exhibit no hydrogen production after the first cycle.

The effect of SiO₂ and CeO₂ particles on the hydrogen production was first evaluated using a MnFe₂O₄:Na₂CO₃ mixture. The addition of CeO₂ has a positive impact on the cyclability. It stabilizes the hydrogen production after the second cycle around 0.05 mmol H₂/g_{mixture}. In turn, the addition of SiO₂ has a negative impact on the cyclability: no hydrogen was produced after the first cycle.

3.2 Characterization of the mixtures

The result of the XRD analysis of the mixtures with mixed carbonates and with SiO₂/CeO₂ particles are shown in Fig 1 and 2, respectively.

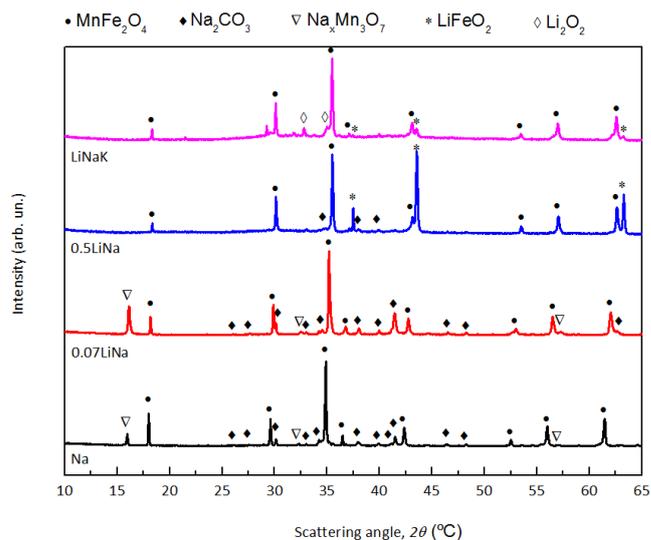


Fig. 1. X-Ray diffraction patterns for the different carbonate mixtures, Na, 0.07LiNa, 0.5LiNa and LiNaK.

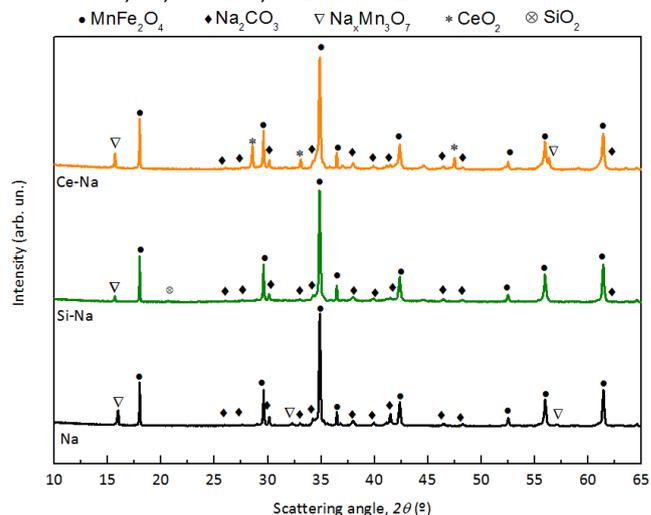


Fig. 2. X-Ray diffraction patterns for the different mixtures with SiO₂ and CeO₂ particles, Na, 0.07LiNa, Si-Na and Ce-Na.

Regarding the carbonate substitution, i.e. 0.07LiNa, 0.5 LiNa and LiNaK mixtures, the XRD analysis suggests that the loss of cyclability is due to the formation of substoichiometric phases that prevents a return to the initial form of the material. In general, the less the Na₂CO₃ content in the mixture, the higher amount of substoichiometric phases is formed.

As Alvani reports [4], it is reasonable to consider that the presence of substoichiometric phases decreases the cyclability in terms of hydrogen production. Nevertheless, it seems to be another reason behind the loss of cyclability, as there is no direct relation between the amount of the secondary phases and the H₂ yield of the different mixtures. For instance, the Na-SiO₂ shows the lowest amount of non-stoichiometric phases but poor reversibility in terms of hydrogen production.

Complementary analysis are necessary in order to discover the reason behind the loss of cyclability. In order to gain information of the material at a microscopy level, characterization techniques such as SEM-EDX and HR-TEM will be carried out. Moreover, the combined effect of

CeO₂/SiO₂ and the use of mixed carbonates is currently under investigation.

4. Conclusions

The substitution of Na₂CO₃ by carbonate mixtures did not improve the cyclability of the process in terms of hydrogen production. However, the 0.07LiNa mixture exhibits the fastest reaction kinetics and highest cyclability in terms of mass variation.

The addition of CeO₂ improves the cyclability in terms of hydrogen production whereas the addition of SiO₂ has a negative impact.

The XRD analysis suggests that the formation of sub-stoichiometric phases might cause the loss of cyclability in terms of hydrogen production. However, a direct relation between the phase composition and the H₂ yield of the different mixtures was not found. Further analysis are being carried out in order to clarify this point.

Acknowledgements

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