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Mn-based oxides modified with MnSiO₃ for thermochemical energy storage



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ABSTRACT

Affordable and durable metal oxide thermochemical energy storage (TCES) materials possess the capability to meet the large-scale energy storage requirements of next-generation concentrated solar power (CSP) plants. Irondoped manganese oxide has garnered increasing attention owing to its non-toxicity, low cost, and high energy capacity at temperatures exceeding 800 °C. However, the challenge of sintering at high temperatures has posed difficulties in maintaining the excellent performance of thermal storage materials over long-term cycles. This study introduces the surface modifier MnSiO₃ into Mn-based oxide (Mn_{0.8}Fe_{0.2})₂O₃ to inhibit grain agglomeration. The effects of preparation methods and silicon precursors on the properties of synthesized MnSiO₃ are investigated. The sample doped with 1 wt% MnSiO₃ demonstrates excellent conversion rate during cycling and retains 94.9 % of its heat storage capacity after 1000 redox cycles. Characterization techniques indicate that MnSiO₃ adhered uniformly to the surface of Mn-Fe oxides without forming any new phase even after 1000 redox cycles. By performing density functional theory (DFT) calculations, the higher formation energy and migration barrier for Mn vacancies are determined, thereby confirming the anti-sintering effect of MnSiO₃ at high temperature. And the interaction between the surface modifiers and Mn-Fe oxides is analyzed, providing a deeper understanding of the long-term stable adhesion mechanism at their interface. This study guides performance improvement and modification design for Mn-based metal oxides while also laying a solid foundation for the large-scale practical application of cost-effective and high-temperature thermochemical energy storage materials.

1. Introduction

The efficient utilization of zero-carbon renewable energy sources, with solar power as a representative example, is a crucial pathway towards achieving decarbonization of industrial heat [1-4]. Given the intermittent and variable nature of these energy sources, the integration of low-cost and high-temperature Thermochemical Energy Storage (TCES) in the next-generation Concentrated Solar Power (CSP) plants holds significant promise for realizing carbon neutrality in the future [5,6]. TCES relies on reversible chemical reactions to store chemical energy, and extensive research has been conducted on various systems such as hydrides, hydroxides, carbonates, and oxides [7]. Among them, metal oxide systems with gas-solid reactions, utilizing air as both the heat transfer fluid (HTF) and carrier of the reactant O2, eliminate the need for additional gas storage devices and provide flexibility in energy storage capacity [8]. Moreover, their operating temperatures are compatible with CSP plants, and higher thermal storage temperatures (>800 °C) can effectively enhance system efficiency. Therefore, these metal oxide systems hold great potential to become the preferred materials for the next generation of CSP systems.

Several studies have identified the development potential of metal oxide pairs, including Co₃O₄/CoO, CuO/Cu₂O, and Mn₂O₃/Mn₃O₄, in the temperature range of 700 to 1100 °C [9–14]. Among these pairs, Mn₂O₃/Mn₃O₄ has garnered significant interest due to its comparative affordability, abundance, non-toxicity, and environmental sustainability. Although it suffers from sluggish oxidation kinetics caused by sintering [15], researchers have effectively addressed this challenge through the introduction of a variety of metal ions (Fe, Cu, Li, Zr, Zn, Ni, Cr, Ti) [16]. Notably, their work demonstrates the remarkable enhancement achieved by Fe-doping, enabling complete re-oxidation in the first reaction cycle. The close similarity in ionic radii between Fe and Mn ions contributes to the observed performance improvement, and the low cost of Fe further accentuates the potential for extensive applications of Mn-Fe oxides, thereby attracting considerable attention [15,17,18]. A series of studies conducted by Carrillo et al. have proposed that the introduction of Fe enhances the energy storage density of Mn-

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based metal oxides, reduces the hysteresis in redox temperature, and improves the oxidation reaction rate. This serves to counterbalance the adverse effects caused by sintering, despite the inevitability of its occurrence [15,19,20]. In the research conducted by Al-Shankiti, it was discovered that the addition of Fe₂O₃ to Mn₂O₃ in a molar ratio of 2:1 demonstrated favorable reaction kinetics [21]. Wokon et al. studied manganese-iron oxides with a molar ratio of 3:1, examining their kinetic and thermodynamic properties. The material demonstrated excellent reversibility and maintained stability throughout 100 redox cycles. It was also observed that the oxidation reaction rate decreased gradually after each cycle [17]. Xiang et al. achieved impressive thermal performance by doping 20 mol% Fe, and they conducted a thorough investigation into its reaction characteristics and microscopic mechanisms and discovered that the core-shell $MnFe_2O_4@Mn_{2.7}Fe_{0.3}O_4$ structure was self-assembled during the reduction process, effectively enhancing the reaction kinetics during the oxidation process [18]. Experimental results showed that a honeycomb module made of (Mn_{0.8}Fe_{0.2})₂O₃ retained 85 % of its capacity after 100 heat storage and release cycles [18]. Based on the aforementioned research, it can be seen that Mn-based composite metal oxides, represented by (Mn_{0.8}Fe_{0.2})₂O₃, stand out for their excellent performance in terms of reaction rate, reaction enthalpy, and reversibility [19]. However, repeated redox cycling leads to an inevitable sintering issue, causing a significant decline in the conversion rate of re-oxidation reactions, reaction rate, and thermal storage density. This severely impacts the feasibility of utilizing manganese-based oxides as thermal storage materials coupled with CSP systems. In practical applications, a lifespan of 100 cycles falls far short of the requirements for energy storage systems in CSP plants. Therefore, improving the durability and cycle stability of thermal storage materials is paramount for ensuring the stability of system operation and reducing operational costs.

One approach to mitigate the sintering issue in Mn-based oxide thermochemical energy storage materials is the incorporation of dopant atoms, which could induce the formation of charge imbalances, disorder, or vacancies, which can facilitate the diffusion of oxygen through the crystal lattice [15]. On this basis, studies have explored doping with modifiers to manganese iron oxide to optimize stability and reaction characteristics further. Preisner et al. ameliorated the high agglomeration tendency of energy storage materials by introducing inert modifiers into Mn-Fe oxides [22]. The inclusion of CeO2 and ZrO2 enhanced the wear resistance of thermal storage particles, whereas the addition of TiO₂ had a serious negative effect on the chemical reactivity of Mn-Fe oxides. Furthermore, similar strategies have been employed in various other application domains. Chen et al. added 60 wt% Al₂O₃ to MnFe₂O₄ to reduce sintering during Chemical Looping Gasification [23]. After 10 cycles, the gasification efficiency decreased by less than 2 %, demonstrating the excellent stability of manganese iron oxide. The introduction of Al₂O₃ created new bonds at the Fe-O-Al interface, preventing agglomeration and preserving the reactivity of Fe-based oxygen carriers (OCs) [24]. Azimi et al. conducted experiments by adding 40 wt% of MgAl₂O₄, CeO₂, ZrO₂, and Y₂O₃-ZrO₂ separately to (Mn_{0.75}Fe_{0.25})₂O₃, aiming to enhance the mechanical strength of Mn-Fe oxides for its application in Chemical Looping with Oxygen Uncoupling (CLOU) [25]. Among these additives, MgAl₂O₄ was found unsuitable due to its reaction with manganese-iron oxides at high temperatures. ZrO2 showed potential but required lower calcination and operating temperatures. Abián et al. preferred doped 7 wt% TiO2 of (Mn0.55Fe0.45)2O3, which showed good mechanical strength and maximized both the deoxygenation and oxygen transport capacities [26]. Miller et al. conducted experiments by loading different ratios of Mn-Fe oxides onto Al-Si-based fluid catalytic cracking catalysts (Si/Al = 0.99) and performing 15 cycles of testing [27]. The experiments demonstrated that the oxygen transfer efficiency was highest at 900°C for the 0Fe100Mn sample loaded on the carrier, reaching 85 %. In addition, Chen et al. [28] utilized doped ferrite (the doped elements include Co, Mn, Sr, and Ce) to achieve twostep thermochemical water splitting for hydrogen production and

demonstrated that the addition of SiO_2 support can disperse ferrite and alleviate high-temperature sintering. After 9 redox cycles, oxygen and hydrogen release performance remained relatively stable, indicating that the active phase remained highly dispersed by SiO_2 even after multiple high-temperature treatments.

In summary, while the stability of particles and modification of metal oxides have been extensively studied in the field of chemical looping, the different operating conditions and application scenarios in chemical looping and thermochemical energy storage result in different deactivation mechanisms for materials [29-31]. Previous research on modifying agents has mainly focused on enhancing mechanical strength, with limited efforts in improving the redox cycle life. Therefore, in order to better address the sintering issue of TCES materials and improve the cycle life of Mn-Fe oxides, this study introduces MnSiO₃ modifiers on the surface of (Mn_{0.8}Fe_{0.2})₂O₃, which not only preserve the original excellent thermal properties of manganese-iron oxides, but also enhance their long-term cycle reversibility and resistance to sintering. The choice of (Mn_{0.8}Fe_{0.2})₂O₃ was based on earlier studies by our team [18]. Furthermore, our team attempted to incorporate the traditional antisintering agent SiO₂ for modification on existing manganese-iron oxide. Although SiO₂ has shown a certain degree of anti-sintering property in previous reports in other fields [32–34], long-term cycling (>100 cycles) still resulted in irreversible capacity loss and the formation of Mn-Si composite metal oxides [35,36]. Therefore, to avoid consumption of reactants and enhance the effectiveness of the anti-sintering additive, we propose an enhanced silica-based modifier that is based on existing research. This modifier demonstrates high-temperature stability, avoids the introduction of new cationic impurities, and has been rarely reported in the field of thermal energy storage (TCES). In the present work, manganese-iron composite metal oxides modified with MnSiO₃ as modifiers are synthesized, and the reactivity performance and cycle life are tested through a series of characterization methods. In addition, by combining density functional theory (DFT) calculation, the anti-sintering mechanism of the composite metal oxides and the interaction between the surface modifier and the metal oxides are elucidated.

2. Material and methods

2.1. Material synthesis

The fresh modified Mn-based thermochemical energy storage materials consist of bixbyite-type $(Mn_{0.8}Fe_{0.2})_2O_3$ (MF) as well as synthesized MnSiO₃ modifier (MS) with low loading (0.1 ~ 10 wt%). As in our previous work, the redox reactant $(Mn_{0.8}Fe_{0.2})_2O_3$ is synthesized by the sol–gel method [18]. MS is prepared by the sol–gel method, solid phase synthesis, and hydrothermal synthesis. In this paper, we focus on the sol–gel method, and the latter two synthetic methods are described in detail in the supplementary material.

2.1.1. Preparation of MnSiO₃ modifier

The synthesis of MnSiO₃ modifier via sol–gel method requires Mn $(NO_3)_2$ (50 %, Sinopharm), Si(C₈H₂₀O₄)(Silicon acetate, 98 %, Sigma Aldrich), citric acid(AR, Sinopharm), and ethylene(AR, Sinopharm). The molar ratio of Mn(NO₃)₂ and Si(C₈H₂₀O₄) is set as 1:1, and the mixture is stirred at a constant speed of 70°C for 3 h. Afterward, a certain amount of EG is added and stirred at 90°C for another 2 h to obtain the gel. The gelatinous mixture is calcined for 3 and 4 h at 400 and 800 °C, respectively, to eliminate the nitric oxide as well as organics and form MnSiO₃.

2.1.2. Assembly of reactants and modifiers

Modified Mn-based oxide heat storage material with attachment modifiers is obtained by solid phase synthesis. MS and MF with different mass ratios are weighed and mixed in a planetary ball mill for 30 min. In this work, MF stands for ($Mn_{0.8}Fe_{0.2}$)₂O₃, MS stands for MnSiO₃ while 0.1MS, 0.5MS, 1MS, 3MS, 5MS, 7MS, and 10MS stand for MnSiO₃ and ($Mn_{0.8}Fe_{0.2}$)₂O₃ mixing ratios of 0.1:99.9, 0.5:99.5, 1:99, 3:97, 5:95,

7:93, and 10:90 wt%, respectively. The specific doping ratio of composite materials is shown in Table 1.

2.2. Materials characterization methods

Structural, morphological, and thermal characteristics of the different samples were determined by a variety of techniques involving X-Ray diffraction (XRD), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Fourier transform infrared (FTIR), and Xray photoelectron spectroscopy (XPS). The phase composition and crystal structures of the samples were determined using powder X-ray diffraction (XRD) patterns obtained from an X'Pert Powder diffractometer. The instrument was equipped with a Cu K α radiation source ($\lambda =$ 1.5406 Å) and operated at 40 kV and 40 mA. The scanning rate was 0.02° , and the most informative data was recorded within the 20 range of 10-80°. Thermal characteristics research of the material was conducted using a Mettler Toledo TGA/DSC3 + simultaneous thermal analyzer with an air atmosphere and a gas flow rate of 50 mL/min. Samples weighing 10 mg were placed into 50 µL platinum crucibles for analysis. SEM analysis was performed using a ZEISS Sigma 300 scanning electron microscope, operating in high vacuum mode at 30 kV, to observe the differences in morphology of the different samples and the microscopic evolution before and after hundreds of redox cycles. In addition, energy dispersive x-ray spectroscopy (EDX) analysis was performed on an OXFORD X-max 50 (125 eV) to obtain chemical composition maps of the different observed sample regions. BET surface areas were obtained from N2 adsorption-desorption isotherms done at -196°C using a Micromeritics ASAP 2460 instrument, whose sensibility is 0.01 m^2/g), and calculated by the Brunauer-Emmett-Teller (BET) theory. The structural and bonding information of the material was assessed through Fourier Transform Infrared (FTIR) spectroscopy using KBr pellets on a Thermo Scientific Nicolet iS20 spectrometer. The spectra were acquired within the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. To analyze the species and ratios of O elements on the surface of Mn-based metal oxides, X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha instrument with monochromatic Al Ka radiation (1486.6 eV) which was operated at 15 kV. To calibrate the peak positions of different elements, the binding energy (BE) value of C 1 s at 284.8 eV was employed.

3. Theory/calculation

DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [37,38], with the core electrons described using the projected augmented wave (PAW) pseudopotential and the valence electrons handled using a kinetic energy cutoff plane wave basis set of 450 eV. The Perdew Burke Ernzerhof (PBE) exchange–correlation functional was used with the generalized gradient approximation (GGA) [39]. The Monkhorst-Pack method was employed to generate k-point meshes for both bulk and slab calculations, as presented in Table S5. In

Ta	ble	1

Identification with	different MS	doping	ratios.
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Sample ID ^a	Doping ratio of MS (wt.%) $^{\rm b}$	Composition
MF	0	(Mn _{0.8} Fe _{0.2}) ₂ O ₃
MS	100	MnSiO ₃
0.1MS	0.1	99.9 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 0.1 %
		MnSiO ₃
0.5MS	0.5	99.5 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 0.5 %
		MnSiO ₃
1MS	1.0	99 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 1 %MnSiO ₃
3MS	3.0	97 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 3 %MnSiO ₃
5MS	5.0	95 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 5 %MnSiO ₃
7MS	7.0	93 %(Mn _{0.8} Fe _{0.2}) ₂ O ₃ + 7 %MnSiO ₃
10MS	10.0	90 %(Mn_{0.8}Fe_{0.2})_2O_3 + 10 %MnSiO_3

^a "M" stands for Mn. "F" stands for Fe. "S" stands for Si.

^b Doping ratio(wt.%) = $m(MS)/{m(MF) + m(MS)}$.

order to accurately handle the strong electron correlation effects in Mn and Fe, the DFT + U method was used, where $U_{Mn} = 2.0 \text{ eV}$ and $U_{Fe} =$ 4.5 eV. The total energy convergence criterion was defined as 1.0×10^{-4} eV, and the optimization of atomic positions and geometries was performed until the residual force reached a value below 0.02 eV/Å. To determine the transition state structure of the reaction, the climbing image nudged elastic band (CI-NEB) method was utilized, and the accuracy of all transition state structures was verified through frequency calculations. The COHP analysis was conducted using the Lobster 4.1.0 code, which converts plane wave functions from VASP to local basis set (STO) [40-42]. To ensure accurate COHP analysis, the number of bands was set to the total number of orbitals present in the model during each calculation. (Mn_{0.8}Fe_{0.2})₂O₃ (110), Mn_{2.97}Fe_{0.03}O₄ (100), MnFe₂O₄ (100), and $MnSiO_3$ (-110) were selected as stable low-index surfaces for the computational models in this study. The detailed structural parameters of the slab models are listed in Table S6.

4. Results and discussion

4.1. Characterization of as-prepared MnSiO₃

In this study, the self-made MnSiO₃ modifier was added to Mn-Fe composite metal oxide by solid-phase synthesis method to optimize its performance. A comprehensive discussion on the effects of synthesis methods and silicon precursors on the MnSiO₃ modifier can be found in the supplementary material. The doping amount of MS has a significant impact on the modified material. Fig. 1 and Table 2, respectively, show the XRD patterns, SEM images, and BET surface area data of samples with different doping proportions. As can be seen in Fig. 1a, the samples at different doping ratios are composed of (Mn,Fe)2O3 (ICDD 00-041-1442) and MnSiO₃ (ICDD 00-012-0181). It is worth noting that the intensity of the MnSiO3 diffraction peaks of the 1MS and 5MS samples is weak due to the low doping ratio. The SEM images of the three samples correspond to Fig. 1c-e. Compared with pure MF, the modifier is attached to the surface of the coral-like metal oxide in the form of small spherical particles, and the particles are evenly distributed (Fig. 1b-e). With the increase of the doping ratio, the coverage degree of spherical particles grows significantly. When the doping ratio reaches 10 wt%, the MF surface is almost entirely covered by MS, showing a loose porous structure (Fig. 1e). The BET surface area shown in Table 1 confirms this observation. With the increase of modifiers content, the specific surface area climbs. The BET surface area of pure MF is only $3.90 \text{ m}^2/\text{g}$, and that of 1MS increases to 10.08 m^2/g , while the specific surface area shot up to $25.10 \text{ m}^2/\text{g}$ when 10 wt% MS is doped.

The doping ratio of modifiers has a great influence on the morphology and BET surface area of composite metal oxides. As shown in Table 2, MS has a large specific surface area of $79.73 \text{ m}^2/\text{g}$. Therefore, the BET surface area of modified Mn-Fe metal oxides can be significantly improved by doping nanometer materials MnSiO₃. In addition, the effect of doping ratio is also reflected in the thermal performance, which will be discussed in the next section.

4.2. Thermochemical energy storage performance

4.2.1. Thermal property analysis of as-prepared samples

In this study, MS doped Mn-Fe composition oxides with mass ratios from 0.1 to 10 wt% are set as a test group to compare their energy storage and cyclability performance. As shown in Fig. 2a, the TG curves of prepared samples with different doping ratios are presented, and the test temperature range was 50-1100-700 °C at a heating/cooling rate of 20 °C/min. In the heating process, fresh doped samples start to reduce at a lower temperature of ~ 955 °C (20 °C lower than that of pure MF), and the outstanding reduction rate of pure (Mn_{0.8}Fe_{0.2})₂O₃ is maintained (finished in 4 min). Notwithstanding, the weight changes of the samples will steadily drop when the doping content is added due to the decrease of effective reaction components. The oxidation process commenced at



Fig. 1. XRD patterns(a) and SEM images of fresh samples: (b) MF; (c) 1MS; (d) 5MS; (e) 10MS.

Table 2 Specific surface area of samples with different MS doping ratios.





Fig. 2. Thermal performance comparison of different samples: (a) TG curves in the first redox cycle; (b) reaction conversion in the first redox cycle with different doping ratios; (c) thermal storage density of fresh samples with its error.

approximately 875 °C, effectively reducing the temperature gap between reduction and oxidation. Furthermore, an increase in the doping ratio resulted in an improvement in the onset oxidation temperature. It is noteworthy that regardless of the doping ratio, the oxidation reaction was completed within a timeframe of 6 min. In addition, the surface modifier MnSiO₃ was subjected to separate TGA analysis (as shown in Fig. 2a), and it exhibited almost no weight change, indicating its stability under the experimental conditions. This observation is further supported by the XRD spectrum (Figure S1). Therefore, it can be inferred that the modifier MS does not transform the crystalline phase during the redox reaction of MF, and the modified Mn-based composite metal oxide reacts as in Eq. (1) [18]. In general, the conversion rate is used to characterize the reaction ratio of the reactants (Eq-S2), which is the percentage of reactant that is converted, representing the material's efficiency in heat storage and release during redox reaction [14], and the detailed comparison of the first reaction conversion rate is shown in Fig. 2b. Through the comparison of the conversion rate data, it can be observed more intuitively that with the increase in doping ratio, a partial sacrifice in reaction rate is incurred. When the doping amount does not exceed 1 wt%, the conversion rate of the fresh sample is maintained above 98 %. Moreover, the simultaneous thermal analyzer can also provide DSC curves of the samples, which is used to measure the endothermic and exothermic capacity of samples. By calculating the integrated area of the exothermic/endothermic peaks on the curves, the thermal storage

$$6(Mn_{0.8}Fe_{0.2})_2O_3 \rightleftharpoons 0.706 \cdot MnFe_2O_4 + 3.294 \cdot Mn_{2.7}Fe_{0.3}O_4 + O_2 \tag{1}$$

density of the samples can be obtained. The enthalpy changes of the reaction of the fresh samples with error bars are plotted from the three DSC data as shown in Fig. 2c, and the average enthalpy changes of reduction for MF, 0.1MS, 0.5MS, 1MS, 3MS, 5MS, 7MS, 10MS are 205.2, 205.1, 201.3, 199.6, 186.6, 182.8, 179.2, 172.3 kJ kg⁻¹ and those of the oxidation are 212.9, 211.4, 207.3, 207.7, 188.7, 183.7, 179.6, 165.5 kJ kg⁻¹, respectively. The trend of energy storage density variation with doping ratio is consistent with the conversion rate results, both dropping with improving doping ratio. And the slight disparity in the reaction enthalpy samples can be attributed to the acceptable measurement errors of the instruments used during testing [18].

As analyzed above, a too-high doping ratio leads to a severe sacrifice of redox reaction conversion and thermal storage density, while a toolow (<1 wt%) doping ratio yields negligible effects after long-term cycling. Therefore, a balance needs to be struck between the two to enhance overall performance. Here, the sample with a doping ratio of 1 wt% (referred to as 1MS) proves to be the optimal choice, and further research primarily focuses on it.

4.2.2. Performance comparison

Cyclic tests were implemented to compare the heat storage performance before and after the MnSiO₃ was introduced. We conducted cyclic tests in a tube furnace and set temperature control programs as a ramp rate of 10 °C min⁻¹ to 1000 °C and maintained at 1000 °C for 10 min to make sure the samples complete reduction; after that, cooled down to 700 °C at the same ramp rate. Figure S4c shows the contrast of the thermal performance of MS and 1MS after their 100th redox reaction. The testing temperature was first ramped up to 1000 °C at 20 °C min⁻¹ and maintained at this temperature for 10 min before being cooled down to 700 °C at 10 °C min⁻¹. It is worth noting that a higher test temperature (e.g., 1100 °C) may be chosen in some literature [8,17,18,43]; nevertheless, in order to avoid unnecessary sintering of the material at higher temperatures [44], the highest testing temperature set in this paper is 1000 °C, and maintain isothermal temperature for 10 min to ensure complete reduction. Through the previous comparison in Fig. 2a, MF and 1MS show similar reaction times and conversion rates at the first cycle, indicating that adding modifiers will not affect energy storage materials' heat absorption and release performance at the first redox cycle.

After 100 cycles, powder caking can be observed in crucibles containing MF sample (Figure S4d), while the 1MS sample remains loose. According to the TG curves (Figure S4c), the reaction temperature and reduction conversion of MF and 1MS after 100 cycles have subtle distinct, but their oxidation performance varies significantly. The onset temperature of reduction/oxidation is 957 °C/861 °C and 955 °C/ 854 °C, respectively, and the reduction conversion rates are 97.80 % and 98.08 %, respectively. However, the oxidation rate of MF after 100 cycles descends considerably, and the reaction time goes up to 20 min or more. At the same time, the oxidation conversion rate is less than 80 %, and the loss of re-oxidation capacity also results in a decrease in heat storage density. The MF sample undergoes severe sintering, which can be attributed to surface densification and pore structure collapse caused by high-temperature exposure, resulting in a gradual decrease in the re-oxidation rate [13]. In comparison, 1MS sample greatly improves re-action time and conversion rate. After 100 cycles, the recovered mass of 1MS maintains 100 %; that is, the materials undergoing the reduction reaction can be wholly re-oxidized in minutes, representing a significant performance improvement over MF.

The comparison of redox reaction properties of Mn-Fe composite metal oxides, as summarized in Table 3, indicate that the modified additives proposed in this study are innovative and have a significant impact on enhancing the anti-sintering performance and cycling stability of manganese-iron metal oxides.

4.3. Cycling life and performance decline trend

To test the performance of anti-sintering surface modifiers in longperiod operation, the cyclic test mentioned in section 4.2.2 was extended to 1000 cycles, and samples were taken every 100 cycles for characterization tests. The thermal properties, crystal phase, and morphology evolution of 1st to 1000th cycles are presented in Fig. 3, and the redox reaction kinetics analysis of 1MS after 0th, 500th, and 1000th cycle is in the supplementary material. As shown in Fig. 3a, the samples are all composed of (Mn,Fe)₂O₃ (ICDD 00-041-1442) and MnSiO₃ (ICDD 00-012-0181), with no phase composition changes during 1000 cycles. The testing temperature was set as follows: heating from 50 °C to 1000 °C, holding at 1000 °C for 10 min, and then cooling down to 700 °C. The heating rate was 20 °C min⁻¹, while the cooling rate was 10 °C min⁻¹. What is interesting about the data in Fig. 3b-c is that the introduction of modifiers makes the material show excellent cycle stability with a remained capacity to be 94.90 % in 1000 cycles. The redox conversion rate during 1000 cycles and the decay fitting formula are presented in Fig. 3c. After 1000 cycles of redox reactions, the conversion rates of reduction and oxidation reactions for 1MS were found to be 94.9 % and 94.5 %, respectively. By fitting the conversion rate data from 1000 cycles to a decay curve, it was observed that the decay trend is almost linear, and the reduction reaction exhibits a slow decay with a slope of 0.0029 %. Referring to this trend, it can still maintain about 80 % heat storage capacity at the 6000th cycle.

To be more prominent, we chose 1MS to carry out SEM to study the effect of MnSiO₃ modifier on microstructural evolution during cyclic redox reactions, presented in Fig. 3d–h. In the first 100 cycles, due to the grain boundary diffusion, the attached modifier formed the globular end of coral morphology, which can be verified by chemical element mapping in Figure S6. During the cyclic evolution, typical coral shapes are formed, and no noticeable morphological changes occur during 1000

Table 3

Comparison of redox reaction properties of Mn-Fe oxides. Performance evaluation indicators refers to the thermal storage capacity when not explicitly specific	ea.
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The ratio of Mn to Fe	Modified additive	Appending proportion/%	Preparation method	Reduction/Oxidation temperature	Performance evaluation indicators	Ref.
3:1	-	-	Dry physical mixing	983 °C/825 °C	The oxidation time is doubled (100cycles)	Wokon et al. [17]
7:3	TiO_2 , ZrO_2 , or CeO_2	20 wt%	Dry physical mixing	- ~971 °C/895 °C ~971 °C /889 °C	$TiO_2(deactivation); ZrO_2(92.1 \%, 30 cycles); CeO_2(91.4 \%, 30 cycles)$	Preisner et al. [22]
4:1	-	-	Improved Pechini method	995 °C /882 °C	87 %(25cycles)	Carrillo et al. [15,19]
4:1	-	-	Sol-gel method	978 °C /878 °C	85 %(100cycles)	Our previous work [18]
1:2	Al ₂ O ₃	60 wt%	Sol-gel method	-	Gasification efficiency decrease by 1.96 % (10cycles)	Chen et al. [23]
0:1	aluminosilicate Si/Al = 0.99	60 wt%	-	-	Oxygen transfer efficiency 85 %(15cycles)	Miller et al. [27]
4:1	MnSiO ₃	1 wt%	Sol-gel method	955 °C /875 °C	94.9 %(1000cycles)	This work



Fig. 3. Cyclic test of 1MS for 1000 cycles: (a) XRD pattern of 1MS after different cycles; (b) TG curves of 1st to 1000th cycles; (c) redox conversion of 1st to 1000th cycles and capacity attenuation fitting curve; (d)-(h) SEM images of 1MS after different cycles.

cycles. The apparent mean particle size listed in Table 4 was obtained based on their SEM images, which were averaged from more than 30 measurements, and the particle size distribution is detailed in Figure S7.

A comprehensive analysis of the above characterization test results shows that the intensity of characteristic peaks decreases after long-time cycles, but the doping of modifiers still inhibits agglomeration to a large extent. The inert component $MnSiO_3$ is stably attached to the surface of $(Mn_{0.8}Fe_{0.2})_2O_3$ even after 1000 redox reactions, which effectively blocks the contact between the crystal particles so that the thermal storage material can ensure the activity of Mn-based oxide thermal storage material at working temperature and capable of long-term hightemperature heat storage/release. It is worth noting that in practical applications, the powder is often extruded into particles or modules to serve as a thermal energy storage medium. The actual application scenarios can be more complex due to the high-temperature calcination and other processes experienced during the forming process, which can

Table 4

The mean particle size of MF, MS, and 1MS after 0, 100,400, 700, and 1000 cycles.

Sample	MF	MS	1MS- fresh	1MS- 100c	1MS- 400c	1MS- 700c	1MS- 1000c
Mean particle size∕µm	0.541	0.058	0.963	1.093	1.135	1.228	1.484

potentially affect the rate of material performance degradation. And factors such as attrition, agglomeration, and cost need to be carefully considered (Figure S8). As this work primarily focuses on thermal energy storage materials, the research of thermal storage unit and its application in thermal storage system will be further carried out in the next step.

4.4. Surface chemistry

The atomic bonding was analyzed using FTIR spectroscopy. The detailed spectrum in the range of $400-4000 \text{ cm}^{-1}$ and the magnified plot in the range of 400–1200 cm^{-1} are shown in Fig. 4a–f. The stretching vibrations of Mn-O are commonly assigned to the vibrational bands centered at 490, 521, and 572 cm⁻¹ [45–47]. The peaks around 690 and 961 $\rm cm^{-1}$ corresponded to Fe-O and Si-O vibration frequency, respectively [47]. The literature [48–52] discusses the vibrational frequencies of Si-O-M (M = Mn, Ti, Fe), and it is widely acknowledged that the peak observed around 961 cm⁻¹ should be attributed to the vibration of the Si-O-Mn bond. In the reduced state shown in Fig. 4c-d, two distinct peaks can be observed at 490 cm^{-1} and 600 cm^{-1} , which may be related to the coupling of the Mn-O stretching modes in the tetrahedral and octahedral sites [53,54]. After a redox reaction, the absorbance peaks of both MF and 1MS (Fig. 4e-f) show no significant changes compared to that of fresh samples, indicating the reversibility of the reduction-oxidation reaction. It is worth noting that the Mn-O and Fe-O peak positions in



Fig. 4. Surface chemistry of different samples. FT-IR transmittance spectra: (a) 1MS fresh; (b) MF fresh; (c) 1MS after reduction; (d) MF after reduction; (e) 1MS after oxidation; (f) MF after oxidation. The right side is a magnified view of the FTIR spectra at 400–1200 cm⁻¹, and the labels (a1) to (f1) correspond to the labels (a) to (f) on the left. XPS spectra (O1s): (g) fresh MF; (h) MF after oxidation; (d) 1MS after 100 cycles; (j) fresh 1MS; (k) 1MS after oxidation; (d) 1MS after 100 cycles.

1MS exhibit a slight blue-shift compared to those of the MF sample, suggesting stronger atomic interactions between them [12]. Furthermore, within the entire set of spectra, absorption peaks corresponding to the OH bending mode are observed within the range of 1100–1600 cm⁻¹. Additionally, a broad band is observed in the 2900–3700 cm⁻¹ region, which can be attributed to overlapping O-H stretching modes [55], which is ascribed to the presence of H₂O absorbed by the samples or KBr [56].

Surface composition and oxygen species of different samples are revealed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 4g-l, the O1s spectra corresponding to MF and 1MS have three peaks for 529–530 eV of lattice oxygen (O_L), 530–531 eV of defect oxide or surface oxygen ions (O_D), and 531–533 eV of adsorbed oxygen species (O_A), including hydroxyl (OH⁻), carbonate (CO_3^{2-}) and so on [7,57]. As demonstrated in Table 5, the proportion of lattice oxygen in 1MS has

increased from 67.33 % to 73.34 % compared to $(Mn_{0.8}Fe_{0.2})_2O_3$, leading to the generation of more active sites [58-60]. At the same time, the lattice oxygen binding energy of fresh 1MS (529.38 eV) is higher than that of MF (529.03 eV). The increase in lattice oxygen binding energy implies an enhancement in the oxygen dissociation energy in the corresponding oxide [61], indicating an increase in the stability of lattice oxygen [62]. Therefore, in the case of the fresh sample, 1MS does not exhibit advantages in terms of reaction rate. After 100 cycles, the percentage of lattice oxygen in MF showed a decreasing trend (67.98 % to 66.28 %), whereas compared with the lattice oxygen composition of MF, the lattice oxygen of the 1MS samples before and after 100 cycles always remained at a high percentage (~74%), which indicated that the surface composition was stable, and the reactivity was still maintained at a high level after the redox cycles. In addition, the oxidation rate of 1MS after 100 cycles also showed superiority compared with MF, as shown in Fig. S4c. The composition of the oxygen species determines the properties of the redox reaction and further confirms the cycling stability of the Mn-Fe metal oxides with the introduction of MnSiO₃.

4.5. MnSiO₃ modification mechanism

4.5.1. DFT calculation

In this section, the mechanism of MnSiO₃ alleviating Mn-Fe oxides sintering was revealed using DFT calculation. Based on the above study of the evolution of the crystalline phase during the reaction, the modifier MS remains stable during the heating/cooling process while the MF undergoes reduction/re-oxidation reactions Eq. (1). The crystal structure models corresponding to the MS and MF oxidized/reduced states were determined by XRD, and the respective Mn ion migration energy barriers were compared with the calculated results. And then, the model is built on the most stable (lowest energy) surface of the modifiers and Mn-Fe oxides to calculate the interfacial separation work and to determine the mechanism of interaction. Before building the MF-MS calculation system, the different orientation surfaces of MnSiO₃ should be tested. And the surface energy calculation results of each orientation are listed in Table S4, from which the low-index surface can be determined as {110}. The reference [18] demonstrates that MF self-assembles during reduction to generate core-shell structures MnFe₂O₄@Mn_{2 97-} Fe_{0.03}O₄ and determine the low index surfaces of MF and its reduced state products as {110}, {100}. As the migration of Mn cations leads to the growth and agglomeration of small particles, its continuous migration intensifies the sintering and affects the reaction properties, especially during the reduction process at high temperatures. Therefore, the DFT calculations of Mn vacancy formation energy and migration energy barriers were performed for the oxidized state (Mn_{0.8}Fe_{0.2})₂O₃ (MF), the reduced state Mn_{2.97}Fe_{0.03}O₄ (shell), MnFe₂O₄ (core), and the modifier MnSiO₃ (MS), as shown in Fig. 5. The formation energy of Mn vacancies in Mn-Fe oxides is found to be lower compared to MnSiO₃, suggesting a higher propensity for Mn ion migration in Mn-Fe oxides. Additionally, the migration energy barrier serves as a more direct indicator of the ease of Mn ion migration within the lattice. Fig. 5b clearly shows that the Mn vacancy migration energy barrier of MS (2.92 eV) is much larger than that of MF (2.11 eV), shell (1.45 eV), and core (2.02 eV). Hence, the migration of Mn cations between MS atoms is more difficult. Since grain

Table 5

Oxygen species and surface molar ratio based on XPS results of different samples.

Sample	Lattice O		Defect O		Adsorbed O	
	Peak position (eV)	Surface molar ratio (%)	Peak position (eV)	Surface molar ratio (%)	Peak position (eV)	Surface molar ratio (%)
MF fresh	529.03	67.33	530.33	20.45	531.82	12.22
MF 1cycle	529.06	67.98	530.49	19.70	531.86	12.32
MF 100cycles	528.96	66.28	530.21	20.81	531.59	12.91
1MS fresh	529.37	73.34	530.89	21.60	532.49	5.06
1MS 1cycle	529.16	73.93	530.53	18.86	531.77	7.21
1MS 100cycles	529.55	74.30	530.94	18.85	532.15	6.85



Fig. 5. DFT calculation results: (a) Mn vacancy formation energy and crystal structure evolution of $(Mn_{0.8}Fe_{0.2})_2O_3$ (MF), $MnSiO_3$ (MS), $Mn_{2.97}Fe_{0.03}O_4$ (shell structure of MF reduced state), and $MnFe_2O_4$ (core structure of MF reduced state); (b) Mn vacancy migration energy barrier.

boundary migration is a short-range diffusion process of solids, the diffusion of massive solid atoms leads to grain boundary migration, which is an important factor leading to particle agglomeration. It is worth stating that solid diffusion rate (D) is negatively correlated with the energy barrier ($E_{barrier}$) and positively correlated with the temperature, and the qualitative relationship is expressed in Eq. (2)

$$D \propto \exp(-E_{barrier}/k_B T)$$
 (2)

Where k_B is Boltzmann constant, and T is the absolute temperature. Thus, a higher Mn vacancy diffusion energy barrier implies that the MS crystal structure is stable and resistant to sintering at a higher temperature. In a nutshell, MnSiO₃ blocks the contact of Mn-Fe oxides, limiting the migration of grain boundaries and effectively alleviating the sintering of Mn-Fe oxides.

In addition, DFT calculations were adopted to evaluate the interaction between Mn-Fe oxides and MS during the redox process. As shown in Figure S9a-d, four slab models were constructed, which are $(Mn_{0.8}Fe_{0.2})_2O_3-(Mn_{0.8}Fe_{0.2})_2O_3, (Mn_{0.8}Fe_{0.2})_2O_3-MnSiO_3, Mn_{2.97}Fe_{0.03}O_4-Mn_{2.97}Fe_{0.03}O_4$, and $Mn_{2.97}Fe_{0.03}O_4$ -MnSiO_3, respectively. Since the MF reduction product MnFe₂O₄ is wrapped by the shell structure and not in direct contact with MS, it is not calculated separately. To examine the stability of the interface, we calculate the ideal work of separation, W_{sep} defined as [63]

$$W_{\rm sep} = \frac{(E_{base} + E_{load}) - E_{base-load}}{A}$$
(3)

Where E_{base} is the energy of Mn-Fe metal oxides, E_{load} is the energy of loading material (Mn-Fe oxides or MS), $E_{base-load}$ is the total energy of the combined system, and A is the interface area of the binding surface. The calculation results are listed in Table 6, from which we can see that $W_{sep1} < W_{sep2}$ and $W_{sep3} < W_{sep4}$, indicating that both MF and reduced

Table 6

Calculation results of ideal separated work (Wsep).

Slab model	$W_{sep} (J/m^2)$
(a)MF-MF (W _{sep1})	2.74
(b)MF-MS(Wsep2)	10.01
(c)Shell-Shell (W _{sep3})	1.35
(d)Shell-MS(W _{sep4})	10.71

shell structures are more strongly bound to MS than themselves. Thus, it ensures that MS is firmly attached to the surface of Mn-Fe oxides throughout the redox reaction and guarantees that MS can play a role in inhibiting the self-agglomeration of Mn-Fe composite metal oxide.

In order to understand the stability of the four models constructed in the previous context (MF-MF, MF-MS, Shell-Shell, Shell-MS) and further analyze the interactions between the modifier and Mn-Fe oxides, we calculated the density of states (DOS) and projected density of states (PDOS) for the optimized four models. The PDOS for Mn-3d orbitals, Fe-3d orbitals, O-2p orbitals, and Si-3p orbitals (if present) were analyzed, as shown in Fig. 6a-d. Comparisons reveal that the binding of MF and MS results in changes in the density of states, including shifts in peaks and positions. This provides evidence for electron transfer between the two surfaces. The analysis confirmed the significant orbital overlap between Mn 3d and O 2p orbitals in both the valence and conduction bands, indicating pronounced covalent bonding characteristics. This observation indicates that the reactivity of Mn-Fe oxides is primarily influenced by the Mn-O bonds, aligning with the established mechanisms of redox reactions documented in the literature [18]. Furthermore, the introduction of a surface modifier results in significant alterations in the Bader charges surrounding the Mn atom, underscoring its impact on the electronic structure and reactivity of the system (Figure S9 and Table S7).

Fig. 6e-h display the projected COHP (pCOHP) plots of the shortest Mn-O bonds at the interface in the four mentioned models. The bonding mechanism between the modifier and Mn-Fe oxides can be determined through analysis using crystal orbital Hamilton population (COHP) analysis [64-66]. The Fermi energy level (E_F) not crossing regions of bonding or antibonding states demonstrates the stability of the four models. The strength of the bonding between Mn and O atoms can be analyzed by integrating the COHP below the Fermi energy level. As seen in Fig. 6e-f, for a single Mn atom in the oxidized state, the influence of the majority spin on the band structure's energy is greater than that of the minority spin on the band structure energy. It should be noted that the negative values of ICOHP are due to the use of -COHP as the x-axis. The ICOHP value for the MF-MS model (2.296 eV) is larger than that of the MF-MF model (1.497 eV). The larger absolute value suggests that Mn has a more substantial overlap with the atomic orbitals of O atoms surrounding it [67], indicating that the interaction between MF and MS is much stronger than the interaction between MF and MF. In the reduced state model, electrons with downward spin predominantly influence the Mn-O bonding (Fig. 6g-h). By comparing the ICOHP values (Table 7), it can be inferred that the shell structure interacts more strongly with MS than the self-bonding of Mn2.97Fe0.03O4- $Mn_{2.97}Fe_{0.03}O_4$, which is consistent with the W_{sep} mentioned above. Mn-Fe oxide exhibits more vital interaction with the surface modifier MnSiO₃, which explains its stable adhesion throughout the redox reaction cycles.

Overall, the MnSiO₃ loading on the (Mn_{0.8}Fe_{0.2})₂O₃ surface not only forms a stable structure at high temperature but also ensures efficient reaction of (Mn_{0.8}Fe_{0.2})₂O₃ in long-term cycling and effectively prevents the performance degradation caused by agglomeration. It is further demonstrated that the introduction of modifiers can perform better compared to (Mn_{0.8}Fe_{0.2})₂O₃ alone, which is consistent with the experimental results.



Fig. 6. Total and partial DOS of (a)MF-MF; (b)MF-MS; (c)Shell-Shell; (d)Shell-MS. Crystal Orbital Hamilton Population (COHP) of Mn and O in four computational models: (e)MF-MF; (f)MF-MS; (g)Shell-Shell; (h)Shell-MS. The pCOHPs of the spin majority and minority are represented by the red and blue lines, respectively. The energy axis is scaled relative to the Fermi level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.5.2. Mechanism of sintering resistance

Based on the above experimental results and DFT calculations, the redox mechanism elucidation of the Mn-based oxide with the addition of the anti-sintering surface modifier $MnSiO_3$ is shown in Fig. 7. $MnSiO_3$

maintains phase stability during the temperature rise and fall and does not affect the redox reaction of Mn-Fe metal oxides. When $MnSiO_3$ nanoparticles are uniformly dispersed on the coral-like surface of Mn-Fe oxides, they are tightly bound to Mn-Fe oxides by forming new chemical

Table 7

Integrated Crystal Orbital Hamilton Population (ICOHP) values of Mn-O in four computational models at the Fermi level.

ICOHP (eV)	MF-MF	MF-MS	Shell-Shell	Shell-MS
Spin up	-0.94040	-1.26444	-0.45399	-0.47954
Spin down	-0.55664	-1.03174	-0.86307	-0.98534
Total	-1.49704	-2.29618	-1.31706	-1.46488

bonds at the interface. The interaction between MS and Mn-Fe oxide at the grain boundaries, that is, the Zener pinning force (F_{ZP}) [68,69], will cancel out with the driving force (F_G) of grain growth, and the grain growth is subsequently inhibited [70]. The utilization of dispersed fine particle pinning effect is a widely applied mechanism to impede grain boundary migration, and has been demonstrated as an effective way to enhance material stability at high temperatures [71]. Research indicates that all types of particles exhibit a tendency to reduce or inhibit grain boundary migration [72], with the effectiveness depending on the type of particle characteristics, pinning positions, and particle fraction of nanoparticles. Moreover, particles located on the grain boundaries can exert a stronger pinning effect. The larger the particle fraction, the larger the theoretical value of the pinning force [70]. However, the improvement of particle fraction also means the reduction of the Mn-Fe oxide proportion, and the thermal storage density of the thermal storage material will be negatively affected. Therefore, we experimentally screened the optimal doping ratio to achieve the best anti-sintering effect. During the long redox cycle, the average grain size of Mn-Fe oxides did not grow significantly, and the conversion rate remained 94.9 %, indicating that introducing MnSiO₃ can effectively restrain the sintering of Mn-Fe oxides.

5. Conclusions

In conclusion, we successfully synthesized (Mn_{0.8}Fe_{0.2})₂O₃ with a surface modifier, MnSiO₃, using the sol-gel method with silicon (IV) acetate as the precursor. Taking into account the reaction reversibility and reaction enthalpy, the addition of 1 wt% of MnSiO₃ (referred to as 1MS) was found to be optimal. Furthermore, 1MS demonstrated excellent long-term stability, where the conversion rate after 1000 redox cycles reaches 94.9 %. Through characterization, it was observed that the nanoscale MnSiO₃ particles were effectively pinned onto the surface of (Mn_{0.8}Fe_{0.2})₂O₃, inhibiting crystal growth and ensuring stability. 1MS sample exhibited no significant changes in crystal phase, morphology, or particle size during 1000 cycles, which contributed to maintaining a high level of redox conversion efficiency. Additionally, we fitted the conversion rate data from the 1000 cycles to obtain the decay curve for the 1MS sample, providing insights into its long-term durability as an energy storage material. Furthermore, DFT calculations revealed relatively high formation and migration energies for manganese vacancies in MnSiO₃, confirming its inhibitory effect on Mn ion migration and its alleviating effect on sintering of Mn-Fe oxides. By constructing a theoretical model of MnSiO₃ modifier loaded on the surface of Mn-Fe oxides, we performed calculations for the ideal work of separation (W_{sep}), Bader charge, density of states (DOS), and crystal orbital Hamilton population (COHP), which provide a theoretical basis for the continuous adhesion of MnSiO₃ to the surface during the Mn-Fe oxide cycling process and deepened our understanding of the interaction between Mn-based metal oxides and modifiers. This work offers a cost-effective and eco-friendly option for the development and operation of high-performance thermochemical energy storage materials, and it can be extended to the application of suppressing sintering in other areas involving metal oxides.



Fig. 7. Schematic diagram of redox reaction mechanism of Mn-based oxides with anti-sintering surface modifier MnSiO₃.

CRediT authorship contribution statement

Yan Huang: Conceptualization, Investigation, Methodology, Software, Writing – original draft. **Peiwang Zhu:** Writing – review & editing. **Haoran Xu:** Visualization, Writing – review & editing. **Changdong Gu:** Validation, Writing – review & editing. **Jinsong Zhou:** Funding acquisition, Project administration, Resources. **Gang Xiao:** Funding acquisition, Project administration, Resources, Supervision.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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