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1. Introduction

There is a general agreement that the CO_2 emission resulting from the burning of fossil fuels is one of the major reasons for the climate change.¹⁻³ It is expected that the energy demand will increase further by 53% by 2030, and fossil fuels will still be the dominant source in the next few decades.⁴ In order to prevent these disastrous effects, there is now the need for a continuing and significant global effort to develop new technologies/ processes for CO_2 capture, storage (sequestration) and utilization (CSU).⁵⁻⁹ CSU is believed to be able to significantly reduce the amount of anthropogenic energy-related CO_2 emissions, and contribute to global climate change mitigation.¹⁰ Among all the CO_2 capture technologies,¹¹ great attention has been



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Potassium dititanate ($K_2Ti_2O_5$) was revealed to possess an unexpected, highly reversible CO₂ sorption/ desorption capacity at *ca*. 750 °C, which is promising as a high-temperature CO₂ adsorbent for sorption enhanced hydrogen production (SEHP) processes. In contrast to numerous other adsorbents that are severely sintered during cycles at high temperatures, the CO₂ sorption/desorption cycles over $K_2Ti_2O_5$ exhibited a contrast particle size "break-down" process. The large $K_2Ti_2O_5$ particles gradually breakdown into $K_2Ti_2O_5$ nanofibers after 20 cycles, leading to a very stable CO₂ sorption/desorption performance with very rapid kinetics. A reversible CO₂ capture capacity as high as 7.2 wt% was achieved at 750 °C. Moreover, only 6 min is required for complete CO₂ desorption at 750 °C, indicating that this adsorbent can be practically run with a simple pressure swing sorption scheme. Surprisingly, an interesting structure switching phenomenon between $K_2Ti_2O_5$ and $K_2Ti_4O_9$ caused by CO₂ sorption and desorption was revealed. A detailed mechanism was proposed based on XRD, FTIR, SEM, HR-TEM, and SAED analyses and was further verified by density functional theory calculation. Considering its relatively high CO₂ capture capacity, superior cycling stability, and excellent regeneration ability, we believe $K_2Ti_2O_5$ offers significant potential as a practical, novel high-temperature CO₂ adsorbent.

> devoted to pre-combustion CO₂ capture, particularly the sorption enhanced steam reforming (SESR) processes.¹²⁻¹⁴

> Currently, more than 50 million tons of H₂ are produced annually, of which the majority is provided by a conventional steam methane reforming route because of the maturity of the technology and its favorable economics.15 However, in order to further increase the H₂ production efficiency and lower the CO₂ emission, the SESR process has been developed recently, which is believed to be more economical, energy efficient, and environmentally friendly, as shown in reaction (1).^{12,13} Since this reaction is equilibrium limited, it is impossible to achieve a complete conversion of CH₄ or CO in a single reactor under normal reaction conditions. However, if the CO₂ byproduct can be removed from the gas phase (e.g. by sorption on a solid CO_2 adsorbent), the normal equilibrium limits are removed and a complete conversion can be achieved. In addition, the process produces pure CO₂, which may be compressed and transported for further storage and utilization.15,16 For the above mentioned SESR process, designing proper high-temperature CO₂ adsorbents is crucial for its practical implementation.

> $CH_4(g) + 2H_2O(g) + adsorbent(s) \leftrightarrow$ $4H_2(g) + adsorbent-CO_2(s)$ (1)

> To date, there are mainly three types of high-temperature CO_2 adsorbents that have been reported for SESR, which are

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CaO,^{5,13} Li₂ZrO₃ (alkali zirconates),¹⁷⁻¹⁹ and Li₄SiO₄ (alkali silicates).²⁰⁻²² Although great progress has been achieved with the above three types of adsorbents, each of them still has their own drawbacks, such as thermal sintering, low kinetics, etc. In this contribution, we are reporting the fourth example, K₂Ti₂O₅ (alkali dititanates) as a novel type of high-temperature CO₂ adsorbent. The present work reports the first study on the hightemperature CO₂ capture performance of potassium titanates (K₂Ti₂O₅, K₂Ti₄O₉, and K₂Ti₆O₁₃). Their CO₂ capture capacities were evaluated using thermogravimetric analysis (TGA) at 200-800 °C. The CO₂ sorption and desorption mechanism over the best adsorbent K2Ti2O5 was investigated using XRD, FTIR, SEM, HR-TEM, SAED, and DFT calculations. The kinetics and cycling stability were also evaluated, and all results demonstrate that K₂Ti₂O₅ is a promising high-temperature CO₂ adsorbent for application in SEHP processes.

2. Experimental

2.1 Synthesis of potassium titanates

Three types of potassium titanates, $K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$ were synthesized by the solid state reaction method. Potassium carbonate (Sinopharm Chemical Reagent Co. Ltd.) and titanium dioxide (Sigma–Aldrich (Wuxi) Life Science & Technology Co. Ltd.) were mixed together, and ground into a fine powder in an agate mortar for a certain time. The molar ratios of K_2CO_3 : $TiO_2 = 1:2, 1:4, 1:6$ were chosen for $K_2Ti_2O_5, K_2Ti_4O_9$, and $K_2Ti_6O_{13}$, respectively. After that, they were calcined at 850, 970, and 1080 °C for 10.0 h in air to obtain $K_2Ti_2O_5, K_2Ti_4O_9$, and $K_2Ti_6O_{13}$, respectively, followed by cooling and crushing to fine powders.

2.2 Characterization of K₂Ti₂O₅

Powder X-ray diffraction (XRD) analyses were conducted in a Shimadzu XRD-7000 instrument in reflection mode with Cu Ka radiation and a power of 40 kV \times 40 mA. Diffraction patterns were recorded within the range of $2\theta = 5-80^{\circ}$, with a step size of 0.02°. The morphologies of synthesized potassium titanates were observed using scanning electron microscopy (SEM, Hitachi S-3400N II). Before observation, the dried samples were sputtered and coated with gold for \sim 120 s under an Ar atmosphere. High resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction patterns (SAED) were performed on a JEM-2010F (JEOL, Japan) microscope with an accelerating voltage of 200 kV. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra of the samples were measured using a Bruker Vertex 70 spectrophotometer. The thermal stability of the samples was determined using a Q50 TGA (TA Instruments) in N₂ with a flow rate of 40 mL min⁻¹. Typically, about 40 mg of sample were used for each run. The samples were placed in a Pt sample pan and heated from room temperature to 800 °C with a ramping rate of 10 °C min⁻¹.

2.3 CO₂ capture evaluation

Sorption of CO_2 on $K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$ was determined using a thermal gravimetric method on a Q50 TGA

analyzer. All samples were pre-calcined at 750 °C for 1.0 h under a flow of 100% N₂ to remove the pre-absorbed species. CO₂ sorption experiments were carried out at certain temperatures for 2.0 h (*e.g.* 200, 300, 350, 700, 750, and 800 °C, respectively), and 1.0 atm with a constant flow of CO₂ (40 mL min⁻¹). Temperature programmed desorption (TPD) of CO₂ was carried out with a fixed bed reactor equipped with a tube furnace. The sample was heated up to 800 °C with a heating rate of 5 °C min⁻¹. The desorbed CO₂ was monitored using an on-line quadrupole mass spectrometer (Hiden, UK).

Cycling tests were also performed with a TGA analyzer. Approximately 40 mg of $K_2Ti_2O_5$ were loaded in a Pt pan. Before the cycling test, the sample was heated up to 750 °C at a ramping rate of 10 °C min under pure N₂. In a typical run, the sorption process was tested at 750 °C in CO₂ for 1.0 h. After sorption, the gas was switched to pure N₂ for desorption at 750 °C for 10 min. The CO₂ sorption and desorption cycles were repeated 20 times.

2.4 Calculation details

Theoretical calculations for $K_2Ti_2O_5$ and $K_2Ti_4O_9$ were based on density functional theory (DFT) implemented in the Vienna *Ab Initio* Simulation Package (VASP).^{23,24} The projector augmented wave (PAW) method^{25,26} was used in our calculation and the generalized gradient approximation (GGA) of the Perdew–Burke– Ernzerhof (PBE)²⁷ form was adopted to describe the exchange and correlation potentials. An energy cutoff of 500 eV was employed for the plane-wave basis throughout this work. All energy calculations were done with a Monkhorst–Pack *k*-point mesh of $7 \times 7 \times$ 5 with energy converged to 1.0×10^{-4} eV per atom.

3. Results and discussion

3.1 Synthesis and characterization of potassium titanates

Potassium titanates were synthesized using a simple solid state method, which is suitable for large scale preparation. In order to obtain well crystallized K₂Ti₂O₅, K₂Ti₄O₉, and K₂Ti₆O₁₃, the mixtures of TiO2 and K2CO3 were calcined at 850, 970, and 1080 °C in air for 10.0 h, respectively. Fig. 1(a) shows the XRD patterns of the obtained potassium titanate samples; they all exhibit good consistency with the reported XRD patterns (PDF51-1890, PDF32-0861, and PDF40-0403, respectively). $K_2Ti_2O_5$ possesses unit cell dimensions a = 11.374 Å, b = 3.799Å, c = 6.616 Å, $\beta = 100.1^{\circ}$, the structure satisfies the space group of C2/m. On prolonged sintering of K2Ti2O5, the (001) Bragg reflection is significantly stronger than the (111) reflection, due to texture (preferred orientation) effects. K2Ti4O9 possesses unit cell dimensions a = 18.250 Å, b = 3.791 Å, c = 12.010 Å, and $\beta =$ 106.4°, while K₂Ti₆O₁₃ possesses a monoclinic crystal structure with a = 15.593 Å, b = 3.796 Å, c = 9.108 Å, $\beta = 99.78^{\circ}$, with a space group of C2/m. No impurity reflections were observed in these patterns, suggesting that the as-synthesized K₂Ti₂O₅, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$ are all phase pure. The inset of Fig. 1(a) shows the schematic structure of K₂Ti₂O₅. The titanium atoms are each co-ordinated to five oxygens grouped as a slightly distorted trigonal bipyramid, and this double unit forms an endless string elongated along the y direction. The layers are



Fig. 1 (a) XRD patterns of synthesized $K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$, and the inset shows the schematic structure of $K_2Ti_2O_5$; (b) SEM image of synthesized $K_2Ti_2O_5$; (c) SEM image of synthesized $K_2Ti_4O_9$; (d) SEM image of synthesized $K_2Ti_6O_{13}$.

held together by the potassium atoms. According to theoretical calculation and model simulation for $K_2Ti_2O_5$, the bond distances of the five Ti–O bonds were obtained, which were 1.58, 1.91, 1.98, 1.99, and 1.98 Å, respectively.

The morphology of the synthesized potassium titanates were examined by SEM analysis (Fig. 1(b–d)). Fig. 1(b) indicates that irregular, flat, plate-like crystals of $K_2Ti_2O_5$ with particle size ranging from several micrometers to several-tens of micrometers were formed. $K_2Ti_4O_9$ formed whisker-type particles with an average width of 200 nm and a length of 5 µm, and $K_2Ti_6O_{13}$ exhibited rod-type particle morphology with an average width of 5 µm and a length of 10 µm. The SEM data show that the average particle size for both $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ are much smaller than $K_2Ti_2O_5$.

3.2 Decomposition and carbonation of potassium titanates

The decomposition and carbonation properties of the three potassium titanates were evaluated using TGA analysis in the presence of either N_2 or CO_2 (Fig. 2(a-c)). The TGA profiles of the decomposition processes suggest that all three potassium titanates possess very high thermal stability, with very little weight loss in the temperature range from 50 to 800 °C. For instance, the final weight losses for K2Ti2O5, K2Ti4O9, and $K_2Ti_6O_{13}$ were only 3.0, 0.4, and 0.1 wt%, respectively. This was to be expected since all these samples were synthesized at temperatures higher than 850 °C. For K₂Ti₂O₅, the major weight loss occurred in the temperature range of 50-200 °C, which is attributed to the desorption of surface water. During the carbonation processes, the trends in weight change for $K_2Ti_4O_9$ and K₂Ti₆O₁₃ were similar to those occurring during the decomposition processes. Both K2Ti4O9 and K2Ti6O13 resulted in weight loss, which was 0.5 and 0.2 wt%, respectively, while for K₂Ti₂O₅, it also displayed weight loss in the temperature range from 50-200 °C, and its weight then started to increase above 200 °C, due to the sorption of CO₂, and finally reached about 100.5%. These results demonstrate that the CO₂ sorption capacities of both K₂Ti₄O₉ and K₂Ti₆O₁₃ are very poor, and almost no CO2 can be captured on either of these two potassium titanates. These data also suggest that only K₂Ti₂O₅ has the capability to capture CO₂, particularly in the temperature range of 600-800 °C. This is the first demonstration of CO₂ capture for $K_2Ti_2O_5$. Furthermore, among the different potassium titanates, the CO_2 capture capability is unique to $K_2Ti_2O_5$.

3.3 CO₂ capture performance of K₂Ti₂O₅

The carbonation experiments demonstrated that $K_2Ti_2O_5$ has great potential as a high-temperature CO_2 adsorbent. To illustrate the potential of $K_2Ti_2O_5$ for SEHP processes, its isothermal



Fig. 2 TGA analyses of (a) $K_2Ti_2O_5$, (b) $K_2Ti_4O_9$, (c) $K_2Ti_6O_{13}$ during decomposition (in N_2) and carbonation (in CO_2) processes. (d) The effect of sorption temperature on the CO_2 capture capacity of $K_2Ti_2O_5$, (e) comparison of the CO_2 capture capacity of $K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$ at 750 °C.





Fig. 3 XRD patterns of fresh K₂Ti₂O₅, CO₂-sorbed K₂Ti₂O₅ for 1.0, 5.0, and 10.0 h, fresh K₂Ti₄O₉, bulk K₂CO₃, and the regenerated K₂Ti₂O₅ sample.

CO₂ capture capacity was evaluated. Fig. 2(d) shows the effect of sorption temperature on the CO₂ capture capacity of K₂Ti₂O₅. The highest CO₂ uptake was achieved at around 750 °C. Before 750 °C, the sorption capacity increased with the increase in temperature, with values of 0.62, 1.58, and 1.67 wt% at 200, 300, and 350 °C, respectively. When the temperature was high, the CO₂ sorption capacity was notably improved, and reached 5.0 and 6.4 wt% at 700 and 750 °C, respectively. However, upon further increasing the sorption temperature to 800 °C, the CO₂ sorption capacity started to decrease (4.9 wt%). This is because the sorbed CO₂ started to desorb when the temperature was too high. These data indicate that the optimal CO₂ sorption temperature for K₂Ti₂O₅ is 750 °C. TGA data in Fig. S1⁺ demonstrate that a rapid release of sorbed CO₂ can be achieved within 6.0 min after pure CO₂ was sorbed at 750 °C for 300.0 min. The excellent regeneration ability is also an important advantage for K₂Ti₂O₅. We have also compared the isothermal CO₂ capture capacity of K₂Ti₂O₅, K₂Ti₄O₉, and K₂Ti₆O₁₃ at 750 $^{\circ}$ C (Fig. 2(e)). It shows that only K₂Ti₂O₅ exhibits a rapid weight increase due to CO₂ sorption. The uptake exceeded 6.4 wt% after capturing CO₂ for 2.0 h. However, with the same temperature (750 °C) and time (2.0 h), neither $K_2Ti_4O_9$ nor $K_2Ti_6O_{13}$ exhibited any CO2 capture. These data demonstrate that $K_2Ti_2O_5$ has an excellent CO_2 capture capacity and good potential for SEHP applications.

3.4 CO₂ sorption/desorption mechanism over $K_2Ti_2O_5$

In order to understand the CO_2 sorption and desorption mechanism, $K_2Ti_2O_5$ was exposed to CO_2 at 750 °C for a given time (1.0, 5.0, and 10.0 h), and the structural and morphological changes as a function of sorption time were monitored using XRD, FTIR, and SEM analyses. The XRD data in Fig. 3 clearly show that by the sorption of CO_2 , the structure of $K_2Ti_2O_5$ gradually transformed into $K_2Ti_4O_9$ and K_2CO_3 . With the increase in CO_2 sorption time, the characteristic Bragg reflections of $K_2Ti_2O_5$ disappear and concomitantly, the characteristic Bragg reflections of $K_2Ti_4O_9$ and K_2CO_3 grow in intensity. After CO_2 sorption for 10.0 h, the dominant Bragg reflections at $2\theta = 10.1^{\circ}$ are much weaker and broader than that from a sample of $K_2Ti_4O_9$ synthesized by the traditional solid state route, indicating that the particle size of $K_2Ti_4O_9$ formed by CO_2 sorption is very small. After annealing the sample in pure N_2 at 750 °C, all the characteristic Bragg reflections of $K_2Ti_4O_9$ and K_2CO_3 disappeared and the structure transformed back into $K_2Ti_2O_5$, indicating that the structure transformation is reversible.

The process was also monitored by infrared spectroscopy, as shown in Fig. 4. After CO₂ sorption on K₂Ti₂O₅ at 750 °C for 1.0, 5.0, and 10.0 h, the characteristic peaks of K₂Ti₄O₉ were observed at 517, 771, and 939 cm⁻¹. The peaks at 517 cm⁻¹ and 939 cm⁻¹ were ascribed to the vibration of the Ti=O bond.²⁸ The peak at 771 cm⁻¹ was due to the bridging μ^2 -O–Ti vibration. Upon capturing CO₂, the vibration of CO₃²⁻ was observed at *ca.* 673 cm⁻¹.²⁹ Meanwhile, it is clear that the peaks centred at 1440 and 1050 cm⁻¹ increased in intensity after capturing CO₂.³⁰ The 1430-1460 cm⁻¹ peaks were probably caused by the presence of K₂CO₃.^{31,32} After regenerating the CO₂-sorbed K₂Ti₂O₅ sample with pure N₂, most characteristic peaks of K₂Ti₄O₉ disappeared and a similar FTIR pattern to that of fresh K2Ti2O5 was obtained, due to the existence of peaks at 673 and 771 cm^{-1} , the regeneration process might not be complete. These data further suggest that the CO₂ sorption and desorption over K₂Ti₂O₅ can be explained by a reversible structure switching mechanism between $K_2Ti_2O_5$ and $K_2Ti_4O_9$, accompanied by the formation of K_2CO_3 .

The proposed reversible structural transformation during CO_2 sorption and desorption was also investigated using SEM (Fig. 5). Fresh $K_2Ti_2O_5$ showed flat, plate-like particles with relatively clean and smooth surfaces (Fig. 5(a)). However, after adsorbing CO_2 for 1.0 h, many cracks were found on the surface, indicating that the large particles had begun to disintegrate into



Fig. 4 FTIR patterns of fresh $K_2Ti_2O_5$, CO_2 -sorbed $K_2Ti_2O_5$ for 1.0, 5.0, and 10.0 h, fresh $K_2Ti_4O_9$, bulk K_2CO_3 , and the regenerated $K_2Ti_2O_5$ sample.

smaller pieces. With the increase in CO₂ sorption time, the particles became increasingly rough. After 10.0 h sorption, its structure was completely destroyed and collapsed into nanofibers corresponding to the formation of $K_2Ti_4O_9$ (Fig. 5(b-d)). The formation of nano-sized crystallites of $K_2Ti_4O_9$ is consistent with the XRD analysis. In order to prove that the morphology change is due to the sorption of CO₂, $K_2Ti_2O_5$ was tested under the same conditions (750 °C for 10.0 h) in N₂. Fig. S2† indicates that the morphology of $K_2Ti_2O_5$ treated in N₂, like fresh $K_2Ti_2O_5$, shows large particles with an average size of 5–10 µm.

HRTEM and SAED were employed to further verify the $K_2Ti_2O_5-K_2Ti_4O_9$ structure switching phenomenon during CO_2 sorption/desorption over K₂Ti₂O₅ (JCPDS, PDF51-1890) (Fig. 6). Fig. 6(a) and (b) show the TEM and SAED images of fresh K₂Ti₂O₅ before CO₂ sorption, in which the diffraction spots for the (020), (22 $\overline{2}$) and (20 $\overline{2}$) planes in K₂Ti₂O₅ were observed to be consistent with their interplanar spacing, with the [101] direction as the zone axis. The data confirmed the formation of the single crystals of K₂Ti₂O₅ before CO₂ sorption. Fig. 6(c) and (d) show the TEM and SAED images of freshly synthesized K₂Ti₄O₉. The diffraction spots for the (020), (211), (402), and (422) planes were clearly detected in the SAED pattern with the $[10\overline{2}]$ direction as the zone axis. Fig. 6(e) and (f) show the TEM and SAED analyses of the K₂Ti₂O₅ sample after adsorbing CO₂ for 10.0 h. According to our previous XRD and FTIR analyses, the K₂Ti₂O₅ crystals transform into K2Ti4O9 crystals due to the abstraction of K ions by CO₂. Thus, the CO₂ sorbed K₂Ti₂O₅ sample is expected to exhibit a diffraction pattern of K₂Ti₄O₉. The SAED diffraction pattern in Fig. 6(f) indeed confirmed our proposed mechanism, in which the diffraction spots of the (020) and $[\bar{4}04]$ planes of $K_2Ti_4O_9$ were observed, with the $[10\overline{2}]$ direction as the crystal zone axis.

In order to thoroughly demonstrate that the CO_2 sorption on $K_2Ti_2O_5$ is reversible, *i.e.*, that the formed $K_2Ti_4O_9$ and K_2CO_3



According to the above discussions, a deeper understanding of the CO_2 sorption/desorption mechanism over $K_2Ti_2O_5$ was proposed, as shown in Fig. 7. $K_2Ti_2O_5$ exhibits a unique layered structure in which co-ordinate Ti atoms form a sheet of edgesharing distorted bipyramids; the two-dimensional sheets or layers have the composition $(Ti_2O_5)^{2-}$. The layers are sandwiched by the potassium cations, which afford a curious unsymmetrical environment of eight oxygens, bearing only a superficial resemblance to the cubic site of the perovskite



Fig. 6 HR-TEM images of (a) fresh $K_2Ti_2O_5$, (c) fresh $K_2Ti_4O_9$, and (e) CO_2 -sorbed $K_2Ti_2O_5$ for 10.0 h, and SAED patterns of (b) fresh $K_2Ti_2O_5$, (d) fresh $K_2Ti_4O_9$, and (f) CO_2 -sorbed $K_2Ti_2O_5$ for 10.0 h.



Fig. 5 SEM images of (a) fresh $K_2 Ti_2 O_5$, (b) CO_2 -sorbed $K_2 Ti_2 O_5$ for 1.0 h, (c) CO_2 -sorbed $K_2 Ti_2 O_5$ for 5.0 h, and (d) CO_2 -sorbed $K_2 Ti_2 O_5$ for 10.0 h.



Fig. 7 The proposed mechanism of $K_2 Ti_2 O_5 - K_2 Ti_4 O_9$ structure switching caused by CO_2 sorption and desorption.

structure.³³ Because the molecular size of CO_2 (~0.33 nm) is much smaller than the distance between adjacent $(Ti_2O_5)^{2-1}$ sheets (0.65 nm), it is possible for CO_2 to penetrate into the inter-layers and react with K⁺ located inside the layers at a certain temperature (600-800 °C). The shortage of potassium led K₂Ti₂O₅ to be transformed into K₂Ti₄O₉ with a low K/Ti value. The crystal structure of K₂Ti₄O₉ consists of many structural units connected through aligned TiO₆ octahedra. The four TiO₆ octahedra formed a framework by edge-sharing, and further constructed staggered sheets with a zigzag string by corner-sharing with the interlayer space of 0.88 nm.³⁴ Because K_2CO_3 possesses unit cell dimensions of a = 5.640 Å, b = 9.831Å, and c = 6.874 Å (PDF87-0730), the formation of K₂CO₃ inside the layers finally led the large particles to disintegrate into nanofibers. By removing the sorbed CO₂, the released K reacts with $K_2Ti_4O_9$ once again to form $K_2Ti_2O_5$. This mechanism is also supported by our previous studies, in which we found a similar structure switching phenomenon between K2Ti2O5 and $K_2Ti_6O_{13}$, induced by the gas phase sorption of molecular NO_x or SO₂ at 500–600 °C.^{35,36} With CO₂, the reason K₂Ti₂O₅ changed into K₂Ti₄O₉, not K₂Ti₆O₁₃ is because the binding energy between K⁺ and carbonate ions is lower than that with nitrate/ sulfate ions. Revealing the structural changes during CO₂ adsorption and desorption is not only important for understanding and designing novel CO₂ adsorbents, but is also crucial for practical application. For instance, some key operating parameters, including theoretical CO₂ adsorption capacity, volume and heat changes during adsorption and desorption, and the highest temperature that can be applied, etc., could be estimated from the structural change mechanism.

The energy changes during CO_2 sorption on $K_2Ti_2O_5$ were calculated using density functional theory (DFT), as shown in Fig. 8. The simulation results indicate that after losing two K atoms by adsorbing CO_2 , if the resulting $K_2Ti_4O_9^*$ still maintains its previous structure, the system energy will be increased by 13.8 eV, which makes the system unstable. However, the transformation of $K_2Ti_4O_9^*$ into $K_2Ti_4O_9$ can lead to the system energy being reduced by 50.6 eV and achieving a steadier state. Thus, from the theoretical perspective, the DFT calculation further verified the feasibility of the proposed CO_2 sorption/ desorption mechanism.

3.5 CO₂ sorption/desorption cycling test over K₂Ti₂O₅

For most of the high-temperature CO₂ adsorbents, such as CaO, alkali zirconates, and alkali silicates, the cycling stability is crucial for their practical application. Although their CO₂ capture capacity may be quite high, how to effectively prevent sintering is a major issue in long term use. In this contribution, the long-term stability of K2Ti2O5 during CO2 sorptiondesorption cycles was also evaluated. In order to figure out the desorption conditions and explore the optimal desorption temperature of K2Ti2O5, TPD of CO2 was carried out. After adsorbing CO₂ at 750 °C, the sample was heated from room temperature to 800 °C with a heating rate of 5 °C min⁻¹. The desorbed CO₂ was monitored using an on-line quadrupole mass spectrometer. Fig. 9 shows that CO_2 desorption begins at 600 °C, with a peak temperature of 714 °C. The CO₂ sorptiondesorption cycling test of K₂Ti₂O₅ was evaluated using a typical pressure swing sorption (PSA) process. The sorption was performed with pure CO₂ at 750 °C for 60.0 min and the desorption was performed with pure N_2 at 750 °C for 10.0 min. Fig. 9(b) shows the CO₂ sorption and desorption performance of K₂Ti₂O₅ during 20 cycles. There was no deterioration in the CO₂ uptake over 20 cycles. In contrast, the CO2 uptake gradually increased within the first few cycles, and eventually became stable thereafter. As shown in Fig. 9(b), the CO₂ uptake increased from 3.9 wt% in cycle 1 to 7.2 wt% in cycle 6. After cycle 6, there was almost no change in CO₂ sorption capacity and it was maintained at ca. 7.2 wt%. Although the CO2 capture capacity of K₂Ti₂O₅ is lower than that of CaO, K₂Ti₂O₅ exhibits superb



Fig. 8 The energy change of the CO₂ capture process calculated using the DFT method; $K_2Ti_4O_9^*$ means the intermediate state of $K_2Ti_2O_5$ after the sorption of CO₂.



Fig. 9 (a) TPD analysis of the CO_2 -sorbed $K_2Ti_2O_5,$ and (b) the CO_2 sorption–desorption cycling test over $K_2Ti_2O_5.$

stability during CO₂ sorption–desorption cycles, which is critical for its practical application.

To clarify why the CO_2 capture capacity actually increased with the increase in cycle numbers, the $K_2Ti_2O_5$ samples after cycle 1, cycle 6, and cycle 20 were analyzed using SEM. The XRD data in Fig. 3 demonstrate that after the desorption of CO_2 , the samples will transform back into $K_2Ti_2O_5$. Fig. 10 shows the morphological changes in $K_2Ti_2O_5$ after cycle 1, cycle 6, and



Fig. 10 SEM images of (a) fresh $K_2Ti_2O_5$, and $K_2Ti_2O_5$ after (b) cycle 1, (c) cycle 6, and (d) cycle 20.

cycle 20. Fresh $K_2Ti_2O_5$ shows big plate-like particles with clean and smooth surfaces (Fig. 10(a)), while on increasing the cycle number from 1 to 20, the particles gradually cracked down and formed $K_2Ti_2O_5$ nanofibers (Fig. 10(b–d)). Therefore, the improvement in CO₂ sorption capacity can be attributed to the morphological changes. Such formed $K_2Ti_2O_5$ nanofibers are more favorable for CO₂ sorption than the fresh $K_2Ti_2O_5$ whose particle size is much bigger.

4. Conclusion

In this contribution, in addition to the previously well studied Li₂ZrO₃ and Li₄SiO₄ as high-temperature CO₂ adsorbents, another type of alkali ceramic-potassium titanate, K₂Ti₂O₅, was investigated as a new type of high temperature CO₂ adsorbent, for the first time. TGA analyses in CO_2 (carbonation process) demonstrated that only K2Ti2O5 has the capability to capture CO₂, particularly in the temperature range of 600-800 °C. Isothermal CO₂ sorption tests showed that the optimal sorption temperature for K₂Ti₂O₅ was 750 °C, with a capacity as high as 6.4 wt% after 2.0 h. By utilizing XRD, FTIR, SEM, TEM, and SAED analyses, the mechanism for the CO₂ sorption and desorption over K2Ti2O5 was investigated, which can be explained by a reversible structure switching mechanism between K₂Ti₂O₅ and K₂Ti₄O₉, accompanied by the formation of K₂CO₃ species. The feasibility of the proposed CO₂ sorption/ desorption mechanism was verified using DFT calculations. CO₂ sorption/desorption cycling tests proved that K₂Ti₂O₅ has excellent stability. In contrast to many adsorbents that deteriorate with cycles, the CO2 uptake of K2Ti2O5 gradually increased within the first few cycles, and eventually became stable afterwards (7.2 wt%). We also demonstrated that a rapid release of sorbed CO_2 can be achieved within only 6.0 min. The good CO_2 capture capacity, excellent cycling stability, and rapid regeneration indicate that K₂Ti₂O₅ could be a very promising hightemperature CO₂ adsorbent for the SEHP processes.

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References

- 1 T. J. Crowley and R. A. Berner, Science, 2001, 292, 870-872.
- 2 M. Meinshausen, N. Meinshausen, W. Hare, S. C. B. Raper, K. Frieler, R. Knutti, D. J. Frame and M. R. Allen, *Nature*, 2009, **458**, 1158–1163.
- 3 M. R. Raupach, G. Marland, P. Ciais, C. L. Quéré, J. G. Canadell, G. Klepper and C. B. Field, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 10288–10293.
- 4 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem.*, 2010, **49**, 6058–6082.
- 5 Q. Wang, J. Luo, Z. Zhong and A. Borgna, *Energy Environ. Sci.*, 2011, 4, 42–55.

- 6 M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt,
 S. Brandani, N. Mac Dowell, J. R. Fernández, M.-C. Ferrari,
 R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall,
 A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter,
- M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao and P. S. Fennell, *Energy Environ. Sci.*, 2014, 7, 130–189.
- 7 L. Huang, J. Wang, Y. Gao, Y. Qiao, Q. Zheng, Z. Guo,
 Y. Zhao, D. O'Hare and Q. Wang, *J. Mater. Chem. A*, 2014,
 2, 18454–18462.
- 8 R. S. Haszeldine, Science, 2009, 325, 1647-1652.
- 9 S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954.
- 10 S. Chowdhury, G. K. Parshetti and R. Balasubramanian, *Chem. Eng. J.*, 2015, **263**, 374–384.
- 11 E. Andreoli, E. P. Dillon, L. Cullum, L. B. Alemany and A. R. Barron, *Sci. Rep.*, 2014, 4, 7304.
- 12 D. P. Harrison, Ind. Eng. Chem. Res., 2008, 47, 6486-6501.
- 13 Z. Li, Y. Liu and N. Cai, Int. J. Hydrogen Energy, 2012, 37, 11227-11236.
- 14 J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare and Z. Zhong, *Energy Environ. Sci.*, 2014, 7, 3478–3518.
- 15 H. M. Jang, K. B. Lee, H. S. Caram and S. Sircar, *Chem. Eng. Sci.*, 2012, **73**, 431–438.
- 16 K. M. K. Yu, I. Curcic, J. Gabriel and S. C. Tsang, *ChemSusChem*, 2008, 1, 893–899.
- 17 H. Pfeiffer, C. Vazquez, V. H. Lara and P. Bosch, *Chem. Mater.*, 2007, **19**, 922–926.
- 18 J. I. Ida and Y. S. Lin, Environ. Sci. Technol., 2003, 37, 1999– 2004.
- 19 B. N. Nair, T. Yamaguchi, H. Kawamura and S. I. Nakao, J. Am. Ceram. Soc., 2004, 87, 68–74.

- 20 M. Kato, S. Yoshikawa and K. Nakagawa, *J. Mater. Sci. Lett.*, 2002, **21**, 485–487.
- 21 C. Gauer and W. Heschel, J. Mater. Sci., 2006, 41, 2405-2409.
- 22 K. Essaki, M. Kato and H. Uemoto, *J. Mater. Sci.*, 2005, **40**, 5017–5019.
- 23 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 14251–14269.
- 24 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 25 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, 50, 17953–17979.
- 26 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 27 B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 7413–7421.
- 28 W. Hou, Q. Yan, B. Peng and X. Fu, *J. Mater. Chem.*, 1995, 5, 109–114.
- 29 X. Lv, Z. Chen, Y. Wang, F. Huang and Z. Lin, ACS Appl. Mater. Interfaces, 2013, 5, 11271–11275.
- 30 J. Ortiz-Landeros, C. Gómez-Yáñez and H. Pfeiffer, J. Solid State Chem., 2011, 184, 2257–2262.
- 31 D. Yamaki, T. Nakazawa, T. Tanifuji, T. Aruga, S. Jitsukawa and K. Hojou, *J. Nucl. Mater.*, 2004, **329–333**, 1279–1282.
- 32 E. Carella and M. T. Hernandez, *Ceram. Int.*, 2014, **40**, 9499–9508.
- 33 S. Andersson and A. D. Wadsley, *Nature*, 1960, **187**, 499–500.
- 34 Y. Cao, K. Zhu, Q. Wu, Q. Gu and J. Qiu, *Mater. Res. Bull.*, 2014, 57, 162–169.
- 35 Q. Wang, J. H. Sohn and J. S. Chung, *Appl. Catal.*, *B*, 2009, **89**, 97–103.
- 36 Q. Wang and J. S. Chung, Appl. Catal., A, 2009, 358, 59-64.