

Synthesis and CO₂ Adsorption Characteristics of Lithium Zirconates with High Lithia Content

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Pure monoclinic phase Li₆Zr₂O₇ and rhombohedral phase Li₈ZrO₆ that coexisted with a fraction of Li₆Zr₂O₇, are synthesized by a liquid phase coprecipitation method and characterized by X-ray diffraction, scanning electron microscopy, and thermo-gravimetric analysis. The high-temperature CO₂ uptake properties of both samples are systematically investigated. The temperature effect tests indicate that, in the case of low temperature (<973 K), both of the adsorbents exhibit slow CO₂ uptake rates because of the inhibited diffusion of CO₂ in the solid carbonate shell; while at the temperature above the melting point of Li₂CO₃ (about 983 K), the CO₂ uptake rates are enhanced dramatically for both $Li_6Zr_2O_7$ and Li_8ZrO_6 , and achieved about 12.3% weight gain and 35.0% weight gain within 15 min at 1073 K, respectively. The thermal stability tests indicate that both samples exhibit gradually reduced capacities during the multicycle processes. The analysis of the crystalline structure reveals that the reduced capacities are resulted from the loss of lithia under high temperatures. Finally, the possible adsorption pathways for both monoclinic phase Li₆Zr₂O₇ and rhombohedral phase Li₈ZrO₆ are suggested as well.

I. Introduction

CO₂ is one of the major greenhouse gases and the largest contributor to the global warming effects (about 60% with regard to its amount in the atmosphere),^{1,2} and coal-burning power plant is the major source of CO_2 generation with the typical CO_2 content about 10%–13%^{3,4}; thus, CO₂ adsorption from the flue gas might be an effective approach for CO₂ capture and storage (CCS). Various materials have been proposed as CO₂ captors, including zeolites,⁵ carbon-based adsorbent,⁶ hydrotalcites,^{7,8} and metal oxides.^{9,10} However, as the temperature of the flue gas vent is about 573-773 K depending on various follow-up process of waste heat utilization, it is highly desired to separate CO₂ directly from flue gas at high temperature and the hot CO₂ flow could be used directly for CO₂ reforming of methane for syngas (H₂ and CO) with little heat transfer,⁸ and the adsorbents should generally have high selectivity and adsorption capacity for CO₂ at high temperature, as well as good adsorption-regeneration kinetics and high multicycle stability.¹¹ Li₂ZrO₃ has shown CO2 selectivity and high adsorption capacity of 28.7 acceptor weight percent by operating at 673-973 K based on the reaction (1), in which, the activation of the adsorbent is originated from the chemical reaction between CO₂ and Li⁺ derived from the lithium-based ceramic; hence, the lithium content in the ceramic might have a great effect on the CO_2 adsorption capacity.^{3,4,12–15} The Li/Zr molar ratios of Li₆Zr₂O₇ and Li₈ZrO₆ are 1.5 and 4.0 times higher than that of Li_2ZrO_3 , respectively, and it is possible that they might adsorb more CO₂ than that of Li_2ZrO_3 under suitable conditions.^{16,17} In this paper, the hightemperature CO₂ adsorption–desorption properties of $\text{Li}_6\text{Zr}_2\text{O}_7$ and Li_8ZrO_6 samples are investigated systematically and the possible adsorption pathways are proposed.

$$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$$
(1)

II. Experimental Section

(1) Synthesis of $Li_x Zr_y O_z$ Compounds

The $Li_x Zr_y O_z$ compounds were synthesized using a liquid-phase coprecipitation method, and were designated as LZO-Li6 and LZO-Li8 corresponding to the target products of Li₆Zr₂O₇ and Li₈ZrO₆, respectively. Starting materials including LiOH.H₂O, NH₃ (25% in water) and Zr(NO₃)₄.H₂O (Shanghai Chemical Co., Shanghai, China) were used as received without further purification. Considering the volatility of lithium under high temperature during the calcination process, the initial Li/Zr molar ratios were higher than the stoichiometric amounts in $Li_x Zr_y O_z$ compounds as described in our previous work.^{18,19} The detailed preparation procedures were carried out as following: Definite Zr(NO₃)₄.H₂O and LiOH.H₂O were weighed with appropriate Li/Zr molar ratios (4.5 and 10.0 for LZO-Li6 and LZO-Li8, respectively) and dissolved with deionized water and NH₄OH solution (2.5 wt% NH₃), respectively; After adding the $Zr(NO_3)_4$.H₂O solution to the lithium hydroxide solution drop by drop and heating in an oil bath at 363 K for 12 h with vigorous stirring, the achieved solid mixture was dried at 393 K for 12 h in the oven, and then ground with mortar and installed in an alumina crucible to be calcinated at 1223 K for a definite time (24 h and 72 h for LZO-Li6 and LZO-Li8, respectively).

(2) Characterization Methods

The crystalline phases were identified using X-ray diffraction (XRD, D/max-RB using CuK α Ni-filtered radiation with $\lambda = 1.5406$ Å, Rigaku, Tokyo, Japan), operating at 40 kV, 100 mA, and scanning in the 2 θ range of 10–80°. The relative percentages of different phases presented in the product were estimated from the total area under the most intense diffraction peak for each phase identified, with the assumption that the peak area was proportional to the volume fraction of each corresponding phase.²⁰ The surface morphology was analyzed by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Tokyo, Japan). Samples for SEM were covered with gold to overcome their poor electric conductivity before analysis.

(3) Properties Study of CO₂ Uptake and Thermal Stability

 CO_2 adsorption kinetics and capacity were studied using a thermo-gravimetric analyzer (TGA, SDTQ600, TA instruments, New Castle, DE). About 15 mg samples were placed in the sample pan and heated to the operating temperature with a rate

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of 20 K/min under 100 mL/min in N₂ flow. Then, N₂ flow was switched to pure CO₂ flow for the test of isothermal adsorption properties. Desorption properties were studied by heat treating the CO₂-adsorbed sample under various temperatures in N₂ flow. Thermal stability of samples was studied over consecutive experiments of adsorption–regeneration at appropriate temperatures under CO₂ and N₂ atmosphere, respectively.

III. Results and Discussion

(1) The Characterization of Crystalline Structure

XRD results of LZO-Li6 and LZO-Li8 are shown in Fig. 1. The sample LZO-Li6 is composed of pure monoclinic phase $Li_6Zr_2O_7$ (JCPDS 34-0312, a = 10.45 Å, b = 5.99 Å, and c = 10.21 Å). However, the sample LZO-Li8 is a mixture of monoclinic phase Li₆Zr₂O₇ and rhombohedral phase Li₈ZrO₆ (JCPDS 26-0867, a = 5.48 Å, and c = 15.45 Å), and the proportion of Li₈ZrO₆ and Li₆Zr₂O₇ are about 60.8% and 39.2%, respectively, which are estimated semiquantitatively by calculating from the total area under the most intense diffraction peak of each phase, (11-1) crystal face for monoclinic phase Li₆Zr₂O₇ and (101) crystal face for rhombohedral phase Li₈ZrO₆. It is reported that pure Li₈ZrO₆ is difficult to prepare due to the loss of lithia by volatilization on prolonged heating at temperatures above 1073 K.^{19,21} In addition, the synthesis methods reported generally were carried out under rigorous conditions such as calcination under ultrahigh vacuum.²² In our experimental procedures, a mass of lithia must be sublimated inevitably because the samples are calcinated directly in static air, subsequently, leading to the production of Li₆Zr₂O₇ in the final product.

(2) The Investigation of Surface Morphology

The surface morphology of the $Li_x Zr_y O_z$ products is shown in Fig. 2. Both of LZO-Li6 and LZO-Li8 are made up of large particles with irregularly polyhedron-shaped structures as shown in Figs. 2(a) and (c), respectively. Moreover, the magnified picture shown in Fig. 2(b) indicates that the large particles of LZO-Li6 are built up by amount of small dense particles with size ranging between 1.0 and 5.0 µm, while the sample LZO-Li8 exhibits a bulk covered with many small particles on the surface as shown in Fig. 2(d). It is clear that the aggregation that occurred in the sample LZO-Li8 is more serious than that of LZO-Li6. This may result from the prolonged calcination time and increased calcination temperature conducted for LZO-Li8; in addition, the higher content of lithium in the process of synthesis may further aggravate the occurrence of agglomeration. Anyway, the results obtained suggest that it may be difficult for CO_2 to penetrate the particles,²³ and as a consequence, the reaction rate with CO_2 is expected to be slow for both of the adsorbents produced here.



Fig. 1. X-ray diffraction patterns of LZO-Li6 and LZO-Li8, r(hkl): rhombohedral phase Li₈ZrO₆ crystal face, m(hkl): monoclinic phase Li₆Zr₂O₇ crystal face.

(3) CO₂ Adsorption–Desorption Properties and Pathway of LZO-Li6 Products

The operating temperature is a key parameter to the CO₂ adsorption rate. Figure 3 shows the isothermal adsorption and desorption graphs at different temperatures (773, 923, 973, and 1073 K for adsorption, 1073, 1123, and 1173 K for desorption, respectively). As shown in Fig. 3(a), the sample LZO-Li6 is able to uptake CO₂ in the whole range of temperatures tested, and exhibits a gradually increased uptake rate with the enhancement of temperature. The cases operating at 773 and 923 K present slow CO₂ adsorption rates and poor capacities in the allowed time. It is suggested that the solid carbonate shell is formed on the surface of particles as the working temperature below the melting point of Li₂CO₃ (about 983 K), and consequently limits CO₂ diffusion to the reaction interface during the adsorption process in the lithiumbased ceramics.^{24,25} This fact must be the main reason resulting in the slow uptake rates here. In addition, the large particle size and serious aggregates (as shown in Fig. 2) must also restrict the Li⁺ and O²⁻ migrating through the Li-Zr-O matrix core.^{17,26} As the temperature increases up to 973 K, a skipped enhancement of the adsorption rate can be observed. For 973 K is close to the melting point of Li₂CO₃, the submolten state Li₂CO₃ formed during the adsorption process may improve the CO₂ diffusion in the carbonate shell, and enhance the CO2 uptake rate subsequently compared with that occurring in solid carbonate shell. As the temperature further increases to 1073 K, the CO₂ capture rate is faster and reaches 12.3% weight gain within only about 10 min and then flattened out. This behavior can be explained by a faster CO₂ diffusion in the formed molten state carbonate shell, and is consistent with the previous suggestion. Figure 3(b) shows the CO₂ desorption property investigated at different temperatures in N_2 flow. The results indicate that CO_2 can be released effectively at the operating temperatures, and the CO₂ desorption time could be shorted from 120 to 50 min as the operating temperature increased from 1073 to 1173 K.

In order to detect the detailed reactions occurring during the above-mentioned adsorption processes, the CO2-adsorbed samples gained by heat treating the sample LZO-Li6 in a tubefurnace at different temperatures for 30 min under CO2 atmosphere and then directly cooling to room temperature out of the furnace, are further analyzed using XRD analysis as shown in Fig. 4. In pattern (b), the diffraction peaks of the sample adsorbed at 873 K are mainly made up of monoclinic phase Li₆Zr₂O₇ and a fraction of monoclinic phase Li₂CO₃ (at 21.34, 23.06°, JCPDS 22-1141, a = 8.36 Å, b = 4.98 Å, and c = 6.19 Å). This result indicates that only a small amount of CO₂ has reacted with Li₆Zr₂O₇ within the allowed time at 873 K, and is consistent with the slow rate of CO₂ adsorption at low temperatures illustrated in Fig. 3(a). However, in pattern (c), the diffraction peaks of the sample adsorbed at 973 K are changed significantly compared with that of pattern (a), and mainly composed of monoclinic phase Li_2ZrO_3 (JCPDS 33-0843, a = 5.43 Å, b = 9.03 Å, and c = 5.42 Å), Li₂CO₃ and some unidentified phase (at 18.40°, 23.10°, and 30.48°), while only a trace of peaks of monoclinic phase $Li_6Zr_2O_7$ ($2\theta = 17.24^\circ$) are detected. The diffraction peaks unidentified may be an interphase of Li2ZrO3 because similar patterns are observed during the synthesis processes of Li₂ZrO₃ using LiOH and ZrO₂ in our experiment. In addition, similar XRD patterns of Li₂ZrO₃ were also reported by Iwan et al.²⁷ In pattern (d) (adsorbed at 1073 K), there are no peaks of monoclinic phase Li₆Zr₂O₇ detected, and the diffraction peaks are attributed to only Li2CO3 and Li2ZrO3, indicating that the reaction between CO₂ and LZO-Li6 is complete. Combining the above illustrations, the possible reaction pathway of high-temperature CO_2 adsorption for monoclinic phase $Li_6Zr_2O_7$ could be inferred as in Eq. (2). The theoretical CO_2 adsorption capacity for Li₆Zr₂O₇ is 13.1% weight gain according to Eq. (2), close to the experimental result (12.3% weight gain) analyzed by TG previously:



Fig. 2. Scanning electron micrographs of LZO-Li6 (top) and LZO-Li8 (bottom).



Fig. 3. Adsorption kinetics of CO_2 (a) and desorption kinetics (b) on LZO-Li6 at different temperatures in CO_2 flow and N_2 flow at a rate of 100 mL/min, respectively.

The thermal stability of sample LZO-Li6 is tested with the multicycle method. According to the above analyzed results, the manipulating conditions are set as following: the sample is heated to 1023 K at a rate of 20 K min⁻¹ in N₂ (100 mL/min) atmosphere, following to a switch in the atmosphere to CO₂ (100 mL/min) to uptake CO₂ for 60 min; after this, the atmosphere is switched to N₂ and the temperature is up to 1123 K at a rate of 10 K/min to release CO₂ for 60 min; finally, the temperature is down to 1023 K at a rate of 10 K/min and the atmosphere is switched to CO₂ for the next cycle. As shown in Fig. 5, the adsorbent exhibits fast CO₂ uptake rate in the three cycles, yet the CO₂ adsorption capacities are reduced gradually for the second and third cycles. These results indicate that the sample LZO-Li6 holds weak cycle stability and a low CO₂ adsorption capacity.

To understand the gradually reduced capacity of CO_2 adsorption, the crystalline structure of the samples used for different cycle times are investigated with XRD analysis. The CO_2 -adsorbed samples that underwent different cycle times are gained by heat treating the sample LZO-Li6 in a tube furnace



Fig. 4. The X-ray diffraction patterns of samples derived from LZO-Li6 before and after CO₂ adsorption. (a) Before adsorption, (b) adsorption at 873 K, (c) adsorption at 973 K, and (d) adsorption at 1073 K (\Box , monoclinic phase Li₆Zr₂O₇; •, Li₂CO₃; \bigcirc , monoclinic phase Li₂ZrO₃; \blacksquare , unknown phase).



Fig. 5. Thermal stability of LZO-Li6 during consecutive adsorption-regeneration cycles.

with the same conditions of adsorption and desorption as set in Fig. 5. During the process of multicycle, the samples used for 1, 2, and 3 cycles (corresponding to the points of A, B, and C as shown in Fig. 5) are taken out from the tube-furnace directly, and after cooling to room temperature, are characterized with XRD respectively. As shown in Fig. 6, patterns of (a), (b), and (c) correspond to the samples used for 1, 2, and 3 cycles, respectively. In pattern (a), the diffraction peaks of sample mostly match triclinic phase Li₆Zr₂O₇ (JCPDS 36-0122). However, in patterns of (b) and (c), the peaks are indexed to triclinic phase Li₆Zr₂O₇ and monoclinic phase Li₂ZrO₃, which are identified according to the specific order of peaks intensity, indicating that a mass of Li₂O must be sublimated under high temperature and causes the deficiency of lithium during cycle processes. Thus, the CO₂ desorption processes of sample LZO-Li6 can be suggested as Eqs. (3) and (4). Firstly, Li_2CO_3 is decomposed to CO_2 and Li₂O, which sublimated partly under high temperature; subsequently, part of Li₂ZrO₃ reacts with Li₂O to produce triclinic phase Li₆Zr₂O₇, keeping the superfluous part remaining. Hence, the reduced capacity of CO₂ adsorption during the multicycle processes must result from the loss of lithia under high temperature:

$$\text{Li}_2\text{CO}_3 \to \text{CO}_2 \uparrow + (1 - x)\text{Li}_2\text{O} + x\text{Li}_2\text{O} \uparrow \tag{3}$$

$$Li_2O + 2Li_2ZrO_3 \rightarrow Li_6Zr_2O_7 \text{ (triclinic)} \tag{4}$$

(4) CO₂ Adsorption–Desorption Properties and Pathway of LZO-Li8

Figure 7 shows the CO_2 capture and regeneration properties of sample LZO-Li8 under different temperatures. As shown in Fig. 7(a), the CO_2 uptake rate is slow at 923 K. This may be due



Fig. 6. The XRD patterns of samples derived from LZO-Li6 used for different cycles. (a) One cycle, (b) two cycles, and (c) three cycles. ($\mathbf{\nabla}$, triclinic phase Li₆Zr₂O₇; \bigcirc , monoclinic phase Li₂ZrO₃).



Fig.7. Adsorption kinetics of CO_2 (a) and desorption kinetics (b) on LZO-Li8 at different temperatures in CO_2 flow and N_2 flow at a rate of 100 mL/min, respectively.

to the limitation of CO₂ diffusion in the formed solid carbonate shell and the restriction of ion (Li⁺ and O^{2-}) migration in the aggregated particle at low temperature as described in LZO-Li6. As the temperature increases up to 973 K, a skipped weight gain (about 11.0%) is detected within the initial 5 min; after this, the uptake rate is reduced gradually and reaches another 20.0% weight gain within the following 2 h. This behavior may be due to the thick carbonate shell formed progressively that prolongs the time of CO_2 diffusing to the reaction interface, which will be discussed further in the following section. As the temperature increases up to 1023 K, the CO₂ uptake rate increases significantly and achieves about 35.0% weight gain within 20 min and then flattens out. Furthermore, the uptake rate is much faster for the case at 1073 K and reaches 35.0% weight gain within only 15 min. The fast kinetics of CO₂ adsorption for the cases at 1023 and 1073 K must be due to the formed molten carbonate shell that improves the CO₂ diffusion as described earlier. Figure 7(b) shows the test of CO₂ desorption between 1073 and 1173 K under N₂ atmosphere. The results indicate that the adsorbed CO₂ could be released effectively under appropriate operating conditions, and the CO₂ desorption process could be completed within about 60 min as desorbed at 1173 K. To the best of our knowledge, this is the first time the Li₈ZrO₆ as a high-temperature CO_2 adsorbent is reported up to date.

Figure 8 compares the X-ray diffraction pattern of LZO-Li8 with that of the CO₂-adsorbed and CO₂-desorbed samples gained by the same procedure as that of LZO-Li6. Compared with CO₂-free sample, the sample that adsorbed CO₂ at 923 K (corresponding to pattern (b)) is mainly composed of Li_2CO_3 and monoclinic phase $Li_6Zr_2O_7$, as well as a trace of



Fig. 8. The X-ray diffraction patterns of samples derived from LZO-Li8 before CO₂ adsorption, after CO₂ adsorption, and CO₂ desorption. (a) Before adsorption, (b) adsorption at 923 K, (c) adsorption at 973 K, (d) adsorption at 1023 K, and (e) desorption at 1173 K (\blacktriangle , rhombohedral phase Li₈ZrO₆; \Box , monoclinic phase Li₆Zr₂O₇; \blacklozenge , Li₂CO₃; \bigcirc , monoclinic phase Li₈ZrO₆; \Box , triclinic phase Li₆Zr₂O₇; \blacksquare , unknown phase).

rhombohedral phase Li_8ZrO_6 , indicating that the adsorption reaction mainly occurred between Li_8ZrO_6 and CO_2 at low temperatures. In the point of 973 K, the diffraction peaks are made up of only Li_2CO_3 and monoclinic phase $Li_6Zr_2O_7$ while no Li_8ZrO_6 can be detected. Hence, it can be inferred that CO_2 may react with Li_8ZrO_6 as Eq. (5) during the adsorption processes:

$$2\text{Li}_8\text{ZrO}_6 + 5\text{CO}_2 \rightarrow 5\text{Li}_2\text{CO}_3 + \text{Li}_6\text{Zr}_2\text{O}_7 \tag{5}$$

However, in the case of LZO-Li6, the monoclinic phase $Li_6Zr_2O_7$ has almost completely disappeared in the sample adsorbed at 973 K. This difference may be due to more Li_2CO_3 being produced in LZO-Li8 than that of LZO-Li6 during the CO₂ adsorption process, as revealed in Figs. 3(a) and 7(a); the isothermal CO₂ uptake test at 973 K exhibits that more than 20.0% weight gain was achieved within the initial 30 min for LZO-Li8, while only about 11.0% weight gain for LZO-Li6 was observed. The thicker carbonate shell formed in sample LZO-Li8 may prolong the time of CO₂ diffusing to the interface, and consequently the monoclinic phase $Li_6Zr_2O_7$ in the sample LZO-Li8 could not react with CO₂ effectively in the allowed operating time.

As the temperature increases up to 1023 K, which is above the melting point of Li_2CO_3 , the diffraction peaks of the CO₂-adsorbed sample (corresponding to pattern (d)) mainly comprise of monoclinic phase Li_2ZrO_3 and Li_2CO_3 , similar to the case of $Li_6Zr_2O_7$ illustrated in Fig. 4(c). Thus, the CO₂ adsorption process of sample Li_8ZrO_6 may comprise of reactions (2)



Fig. 9. Thermal stability of LZO-Li8 during consecutive adsorption-regeneration cycles.

and (5), which provides with a high CO₂ adsorption capacity of 54.4% weight gain. Considering the previous XRD analysis that about 60.8% proportion of Li₈ZrO₆ and 39.2% proportion of Li₆Zr₂O₇ are present in the sample LZO-Li8, the total weight addition of LZO-Li8 after CO2 adsorption is about 38.2% calculated by Eqs. (2) and (5), close to the experimental result of 35.0%, further confirming the speculation suggested here. In succession, pattern (e) shows the crystalline phases of the CO₂released sample gained by heating the CO2-adsorbed sample (adsorbed CO₂ at 1023 K for 30 min) at 1173 K for 120 min under N2 atmosphere, and the diffraction peaks comprise of almost pure triclinic phase Li₆Zr₂O₇ except some unknown peaks at 16.70°, 24.14°, and 28.16°, which may be the impurity phase introduced during the CO₂ desorption process. It is reported that the synthesis of Li₈ZrO6 needs a long duration above 1073 K.^{21,22,28} Hence, the short desorption time in this study may lead to only Li₆Zr₂O₇ being produced with no Li_8ZrO_6 in the desorbed sample, and the Eqs. (3) and (4) can also be considered as the possible reaction during the desorption process.

Figure 9 shows the thermal stability of sample LZO-Li8 tested under the conditions adsorbed at 1023 K for 30 min and desorbed at 1173 K for 60 min, respectively. The result indicates that the CO₂ uptake capacity reaches about 35.0% weight gain for the first cycle, and subsequently reduced gradually for the following cycles. For the fourth cycle, the maximum CO₂ uptake capacity is reduced to about 23.5% of weight gain. Combining the XRD analysis in Fig. 8 and the previous explanation in the part of LZO-Li6, the loss of lithia under high temperature must be the main reason for the reduced CO₂ uptake capacity during the cycles.

IV. Conclusions

Pure monoclinic phase Li₆Zr₂O₇ (sample LZO-Li6) and rhombohedral phase Li8ZrO6 that coexisted with a fraction of Li₆Zr₂O₇ (sample LZO-Li8) are synthesized by liquid-phase coprecipitation method and applied as high-temperature CO₂ adsorbents. At the temperatures <973 K, both adsorbents exhibit slow CO_2 uptake rate because of the limitation of CO_2 diffusion in the solid carbonate shell and ion (Li^+ and O^{2-}) migration in the large particles. At temperatures higher than the melting point of Li₂CO₃ (about 983 K), both Li₆Zr₂O₇ and Li₈ZrO₆ exhibit a skipped increase of CO₂ uptake rate with about 12.3% and 35.0% weight gain within 15 min at 1073 K, respectively. The adsorbed samples of monoclinic phase Li₆Zr₂O₇ comprises of monoclinic phase Li₂ZrO₃ and Li₂CO₃, and the regenerated sample comprises of triclinic phase Li₆Zr₂O₇, while the rhombohedral phase Li₈ZrO₆ firstly produces monoclinic phase Li₆Zr₂O₇ during the CO₂ adsorption process, and then proceeds to the same reaction pathways as that of monoclinic phase Li₆Zr₂O₇. The thermal stability tests indicate that both the adsorbents exhibit a gradually reduced adsorption capacity during the multicycle processes because of the volatilization of Li₂O decomposed from Li₂CO₃ under high temperature.

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