

CO₂ capture using dry TiO₂ -doped Na₂CO₃/Al₂O₃ sorbents in a fluidized-bed reactor

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Abstract: In order to improve the reactivity of Na₂CO₃/Al₂O₃ sorbent with CO₂, a new sorbent showing high reactivity was developed by doping Na₂CO₃/Al₂O₃ with TiO₂ using impregnation. Fourteen multi-cycle carbonation/regeneration tests of the sorbent were carried out in a fluidized-bed reactor and the sorbent was characterized by X-ray diffraction and nitrogen adsorption. It is confirmed that TiO₂ shows a positive effect on the adsorption process of Na₂CO₃ and the reaction rate is observed to increase significantly, especially in the first 10 min. Moreover, TiO₂ is stable within the temperature range of the process and no other Ti-compounds are detected. The carbonation products are NaHCO₃ and Na₅H₃(CO₃)₄. The surface area and the pore volume of the sorbent keep stable after 14 cycles. The Fourier transform infrared spectroscopy and the X-ray photoelectron spectroscopy are used to analyze the effect mechanism of TiO₂ on CO₂ adsorption process of Na₂CO₃/Al₂O₃.

Key words: CO₂ capture; Na₂CO₃/Al₂O₃; TiO₂; fluidized-bed test

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Applying alkali metal-based solid sorbents for CO₂ capture from flue gas has been investigated as an innovative concept in these years. K₂CO₃ or Na₂CO₃ can be used as the regenerable solid sorbent based on the chemical absorption process at the low temperature. Most studies around the world focus on the potassium-based sorbents because potassium carbonate is generally superior to sodium carbonate in terms of both CO₂ capacity and kinetics^[1-5]. Nevertheless, the primary advantage of using sodium carbonate over potassium carbonate is due to its low price, easy accessibility, and low CO₂ capture cost. If the reaction characteristics of the sodium-based sorbents can be improved for high reactivity, a high conversion rate, and a short reaction time, this technology will have great market value and broad application prospects.

Researchers have also tried to develop alkali metal-

based sorbents supported on various supports, such as activated carbon, Al₂O₃, SiO₂, MgO, ZrO₂, CaO, and zeolites^[2-3, 5]. Activated Al₂O₃ is confirmed to be an outstanding support for CO₂ capture attributed to its well-developed microstructure and excellent abrasion resistance^[3-4]. A previous study^[6] also demonstrated that sorbent Na₂CO₃/Al₂O₃ (Na₂CO₃ impregnated on Al₂O₃) shows a significant performance for CO₂ capture at a low temperature in the presence of vapor. Whereas the CO₂ absorption rate of the sorbent still needs to be increased.

Recently, increasing attention on the use of doped calcium-based CO₂ sorbents has been paid. Chen et al.^[7] doped limestone with attapulgite and demonstrated that the doped sorbent shows better CO₂ capture performance than the natural limestone under the same condition. Sun et al.^[8] investigated manganese salts, including Mn(NO₃)₂ and MnCO₃, doped calcium-based sorbents and reported that the cyclic CO₂ capture capacity of CaCO₃ was significantly improved. Al-Jeboori et al.^[9] reported that MgCl₂, CaCl₂, and Grignard reagents as dopants can improve the carrying capacity of Havelock limestone in repeated cycles of carbonation and calcination in a fluidized bed reactor. Accordingly, doping is promising for developing advanced alkali metal-based solid sorbents to remove CO₂ more effectively. Whereas little related work has been reported so far.

The principal goal of the present research is to investigate methods to improve the CO₂ uptake rate in such a process by doping TiO₂ in Na₂CO₃/Al₂O₃. The reaction mechanism of Na₂CO₃/Al₂O₃ and TiO₂ doped Na₂CO₃/Al₂O₃ are studied and analyzed. Their carbonation/regeneration characteristics, microstructure and physical properties are investigated in 14-cycle tests using a fluidized-bed reactor.

1 Experimental Section

1.1 Samples preparation

Na₂CO₃ and TiO₂ were provided as analytical reagents, and γ-Al₂O₃ were supplied by the Research Institute of Nanjing Chemical Industry Group. Two sorbents were prepared in this study. Na₂CO₃/Al₂O₃ was named Sorb 1 and TiO₂ doped Na₂CO₃/Al₂O₃ was named Sorb 2. The sorbents were prepared by the impregnation method. Appropriate amounts of sorbent constituents were mixed and impregnated in deionized water, then dehydrated at 378

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K, and calcined at 573 K. The sorbents were ground to appropriate particle sizes (0.18 to 0.315 mm) for fluidized-bed tests. Detailed information about the process can be found in previous work^[10]. Loadings of Na₂CO₃ were maintained around 25% (mass fraction) in the two sorbents. The designed loading of TiO₂ in Sorb 2 was 1% (mass fraction). The rest of the sorbents were Al₂O₃ used as supports. X-ray fluorescence (XRF) was used to determine the actual loadings of Na₂CO₃ and TiO₂. The results are listed in Tab. 1.

Tab. 1 Sorbent components content in mass fraction %

Components content	Sorb 1	Sorb 2
Designed loading of Na	10.85	10.85
Actual loading of Na	9.88	9.98
Designed loading of Ti		0.6
Actual loading of Ti		0.82
Actual loading of Na ₂ CO ₃ and TiO ₂	22.77	24.36

1.2 Apparatus and procedure

A bubbling fluidized-bed reactor was operated for multiple-cycle tests as shown in Fig. 1. The inner diameter of the reactor is 0.05 m and height is 1.0 m. Detailed information was reported in Ref. [3]. The sorbents mounted was about 250 g. The simulated flue gas containing 10% CO₂ and 12% H₂O with a balance of 78% N₂ (volume fraction) was used for carbonate reaction. The flow rate was 750 L/h. The carbonation temperature was maintained at 333 K. After the completion of carbonate reaction, the flue gas was switched to 100% N₂ at a flow rate of 750 L/h as a purge gas. After the purge of CO₂, the temperature of the reactor was raised to 473 K for regeneration. After regeneration, another carbonate reaction was performed by cooling the temperature of the reactor to 333 K. In this way, 14-cycle tests were carried out.

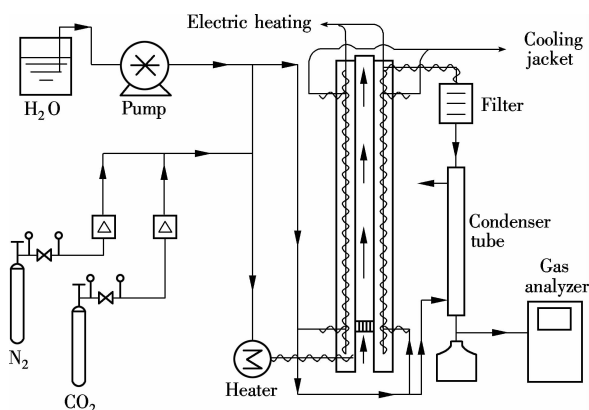


Fig. 1 Schematic diagram of the experimental apparatus for fluidized-bed tests

An APhi 5 000 Versa Probe X-ray photoelectron spectroscopy (XPS) was introduced to examine the type and relative content of the surface elements. The surface spectra of TiO₂ were observed by a NICOLET NEXUS870

Fourier transform infrared spectrometer (FTIR). The surface areas and pore size distributions of sorbents were determined by a micropore physisorption analyzer with nitrogen adsorption-desorption.

2 Results and Discussion

2.1 Fluidized-bed tests

Fluidized-bed tests of Sorb 1 and Sorb 2 were processed successively. A typical carbonation-regeneration single cycle result of Sorb 1 is presented in Fig. 2. The left part of the figure represents the carbonate reaction and the right part represents regeneration reaction.

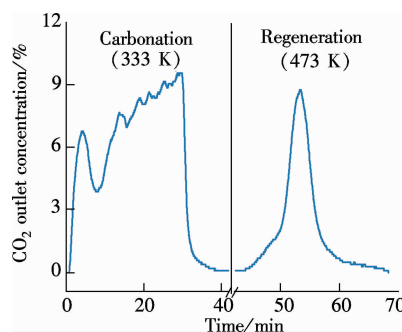
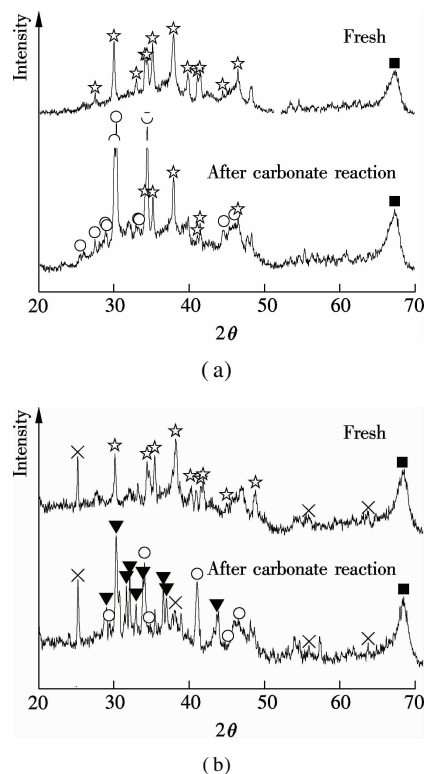


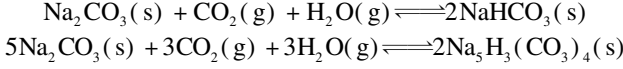
Fig. 2 Fluidized-bed test result of Sorb 1 in carbonation-regeneration single cycle

XRD results of Sorb 1 and Sorb 2 before/after carbonate reaction, as shown in Fig. 3, were provided in a previous work^[10]. It has revealed that the main constituents



☆—Na₂CO₃; ■—Al₂O₃; ○—NaHCO₃; ×—TiO₂; ▼—Na₅H₃(CO₃)₄
Fig. 3 XRD patterns of Sorb 1 and Sorb 2 before/after carbonate reaction^[10]. (a) Sorb 1; (b) Sorb 2

of Sorb 1 before the carbonate reaction are Na_2CO_3 and Al_2O_3 . After the carbonate reaction, the NaHCO_3 phase is observed. The main constituents of Sorb 2 before the carbonate reaction are Na_2CO_3 and TiO_2 , besides Al_2O_3 . After the carbonate reaction, the NaHCO_3 phase and a new product known as Wegscheiderite ($\text{Na}_5\text{H}_3(\text{CO}_3)_4$) are observed. The relevant reactions are



The two reactions are reversible. Furthermore, no Ti-containing compound is detected before/after carbonate reaction except for the TiO_2 phase which coincides with Lee's study^[1].

CO_2 absorbed/desorbed amounts were exhibited by a numerical integration of the CO_2 concentration curve. The amounts of CO_2 absorbed in the whole carbonate reaction n_{ct} , amounts of CO_2 absorbed in the first 10 min of carbonate reaction n_{ci} and amounts of CO_2 desorbed in regeneration n_{r} of the two sorbents are listed in Tab. 2, respectively. Good material balance closure was obtained, which indicates that the absorption of CO_2 is practically reversible on Al_2O_3 support.

Tab. 2 Amounts of CO_2 absorbed and desorbed in each cycle of the two sorbents

Cycle	n_{ci}		n_{ct}		n_{r}	
	Sorb 1	Sorb 2	Sorb 1	Sorb 2	Sorb 1	Sorb 2
1	0.276	0.384	0.509	0.527	0.501	0.515
2	0.258	0.379	0.499	0.513	0.491	0.505
3	0.249	0.362	0.490	0.503	0.481	0.491
4	0.230	0.344	0.467	0.498	0.458	0.482
5	0.235	0.349	0.458	0.491	0.449	0.482
6	0.225	0.354	0.467	0.484	0.450	0.469
7	0.221	0.359	0.450	0.473	0.441	0.462
8	0.206	0.342	0.465	0.476	0.441	0.460
9	0.209	0.320	0.440	0.475	0.423	0.461
10	0.203	0.308	0.444	0.467	0.428	0.451
11	0.205	0.295	0.449	0.465	0.435	0.448
12	0.203	0.293	0.411	0.456	0.392	0.436
13	0.183	0.287	0.439	0.455	0.420	0.442
14	0.182	0.312	0.439	0.455	0.421	0.439

The carbonation capacity of CO_2 A_{c} (milligram of CO_2 absorbed by per gram of sorbent) and regeneration percent conversion η_{r} are used for expressing the carbonation and regeneration characteristics of the two sorbents. They can be calculated by

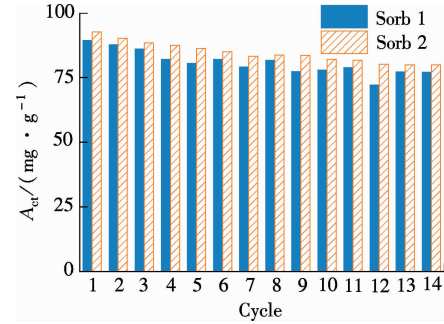
$$A_{\text{c}} = \frac{1000n_{\text{c}}M_{\text{CO}_2}}{w(0)} \quad (1)$$

$$\eta_{\text{r}} = \frac{n_{\text{r}}}{n_{\text{ct}}} \times 100\% \quad (2)$$

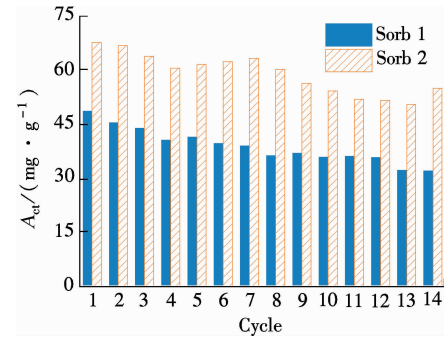
where $w(0)$ is the initial mass of sorbent; M_{CO_2} is the molecular mass of CO_2 .

According to Eq. (1), the carbonation capacity of CO_2

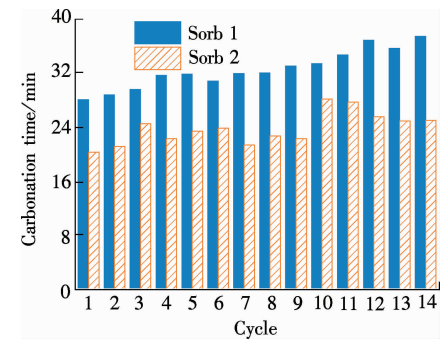
in the whole carbonate reaction A_{ct} and carbonation capacity of CO_2 in the first 10 min of carbonate reaction A_{ci} of the two sorbents are calculated and given in Figs. 4(a) and (b). Lee et al.^[2] reported their potassium-based sor-



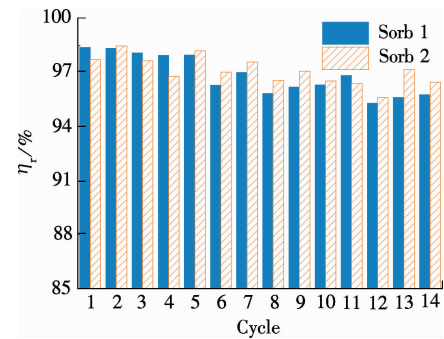
(a)



(b)



(c)



(d)

Fig. 4 Fluidized-bed test results of Sorb 1 and Sorb 2 in multiple cycles. (a) Carbonation capacities of CO_2 in the whole carbonate reaction; (b) In the first 10 min of carbonate reaction; (c) Carbonation time; (d) η_{r}

bents by impregnation K₂CO₃ on Al₂O₃. A_{ct} of their sorbent with 30% loading of K₂CO₃ is about 82 mg/g in the 1st cycle and decreases to about 50 mg/g after 5 cycles. Distinct from their claim, as can be noted from Fig. 4 (a), the A_{ct} of Sorb 1 is between 77 and 90 mg/g in 14 cycles with a quite slow deactivation. As for Sorb 2, A_{ct} is slightly higher than that of Sorb 1 in the 14 cycles.

As can be noted from Fig. 4(b), the A_{ci} of Sorb 1 is around 40 mg/g in each cycle, less than half of the corresponding A_{ct} of Sorb 1. The carbonate reaction rate of Sorb 1 is low. The A_{ci} of Sorb 2 in each cycle is about 0.5 times higher than that of Sorb 1 in each cycle between 55 and 68 mg/g, occupying about 70% of the corresponding A_{ct} of Sorb 2. It suggests that the use of TiO₂ as a dopant can increase the carbonate reaction rate, particularly in the first 10 min. Previous research^[11] reported that the A_{ci} of K₂CO₃/Al₂O₃ is around 50 mg/g in a 4 cycles test. The A_{ci} of our Sorb 2 is higher than that of the potassium-based sorbent. Moreover, the total carbonate reaction time is also shortened in each cycle, as shown in Fig. 4(c), owing to the optimization of the carbonate reaction in the first 10 min.

Lee et al.^[12] reported a novel potassium-based sorbent by impregnation K₂CO₃ on zirconium oxide (ZrO₂). A_{ct} of the sorbent with 30% loading of K₂CO₃ is around 85 mg/g in 10 cycles, showing excellent carbonation/regeneration cycle performance. Its A_{ct} is somewhat lower than the A_{ct} of our sorbents, which can be attributed to the different reactors and absorption atmospheres researched.

With respect to the regeneration section, one can observe from Fig. 4(d) that the η_r of the two sorbents in each cycle are all above 95%, which indicates that the decompositions of NaHCO₃ and Na₃H₃(CO₃)₄ are almost completed within regeneration temperature range and the doping of TiO₂ hardly has an impact on the regeneration part.

2.2 Microstructure change of the two sorbents with cycle numbers

In the fluidized-bed reactor, due to the intense movements of sorbents and chemistry reactions, the microstructure of the two sorbents can be changed after the 14-cycle test. In Fig. 5, the change in the surface area, pore volume and pore size distribution of Sorb 1 and Sorb 2 before/after multi-cycle tests are presented.

As shown in Fig. 5(a), after 14 carbonation/regeneration cycles, the surface area of the two sorbents decreases from 89.72 and 86.75 m²/g to 80.45 and 78.56 m²/g, respectively. The pore volume of the two sorbents decreases from 241.2 and 239.0 mm³/g to 234.5 and 231.1 mm³/g, respectively. The decrements are quite insignificant. In Fig. 5(b), the pore size distributions are consistent during the 14 cycles and the change is small. The excellent microstructure performance is attributed to the usage of Al₂O₃ as support which is consistent with Ref. [3].

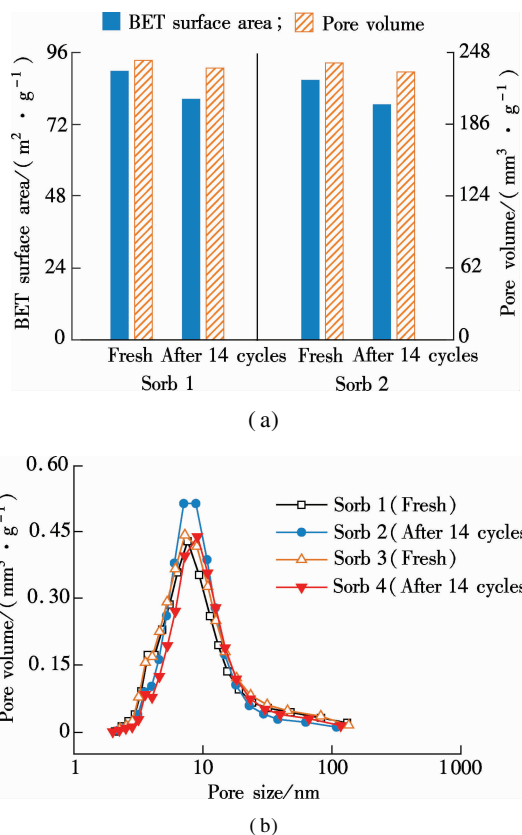


Fig. 5 Structure change of Sorb 1 and Sorb 2 in 14-cycle fluidized-bed tests. (a) BET surfaces and pore volumes; (b) Pore size distributions

2.3 XPS test

In order to reveal the promotion mechanism of TiO₂ on CO₂ absorption, the XPS test of TiO₂ was introduced. As shown in Fig. 6, the O_{1s} photoelectron peak of the TiO₂ surface displayed a broad shoulder which was resolved into two peaks after a numerical fit (dotted lines in Fig. 6). The main peak at 529.4 eV can be associated with the titanate oxygen. The second oxygen peak at 531.0 eV can be assigned to OH groups that likely are incorporated on TiO₂ surfaces when they are exposed to H₂O. These results are in good agreement with the XPS measurements of Nagarkar et al.^[12]

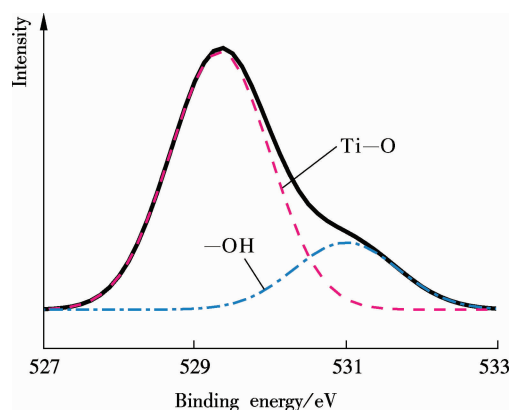


Fig. 6 The XPS spectra of O_{1s} of TiO₂

2.4 FTIR tests

Fig. 7 shows the changes in the FTIR spectra of TiO_2 progressive heated from an ambient temperature to 473 K in the oven. It can be noted that, a large, broad band centered around $3\,300\text{ cm}^{-1}$ is assigned to the vibration of isolated surface OH groups and absorbed water on TiO_2 . A shoulder around $1\,620\text{ cm}^{-1}$ assigned to the vibration of surface OH groups. As the temperature rises, the broad band around $3\,300\text{ cm}^{-1}$ reduces in intensity.

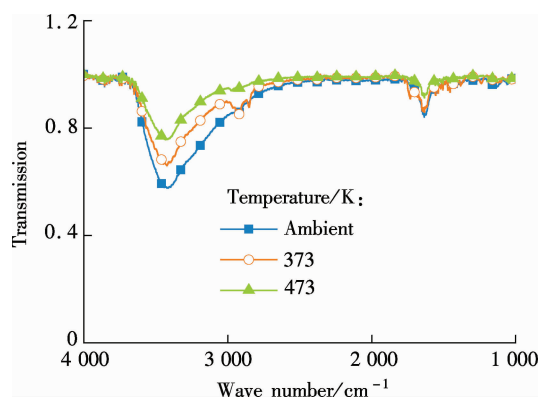


Fig. 7 The FTIR spectra of TiO_2 before and after heat treatment

3 Mechanism Analysis of the TiO_2 -doped $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ Sorbent

The surface property of TiO_2 is decisive for its catalytic application. The reaction activity and selectivity of Na_2CO_3 itself depend directly on the type and concentration of the different active sites.

Zhao et al.^[4] verified that the H_2O adsorption is regarded as the rate-controlling step of carbonation. As the H_2O concentration increases, the diffusion and adsorption capacities of H_2O in the sorbent are improved. Therefore, the total carbonation conversion increases when the H_2O concentration increases.

Takeuchi et al.^[13] pointed out that, as shown in Fig. 8, the H_2O molecules, which directly interact with the solid surface of TiO_2 such as surface cations or surface hydroxyls, form a monolayer as chemisorbed H_2O molecules and then the hydrogen-bonded H_2O molecules form multilayers as physisorbed H_2O molecules. Finally, H_2O molecules without active hydrogen bonds cover the polymeric chained H_2O molecules to form the outermost shell of the H_2O cluster. These polymeric chained H_2O molecules are called “hydrogen-bonded water”, while on the other hand, the hydrogen-bond-free H_2O molecules in the outermost shell are called “free water”.

By doping TiO_2 on $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$, the multilayers of H_2O can be adsorbed on the surface of sorbent. The mul-

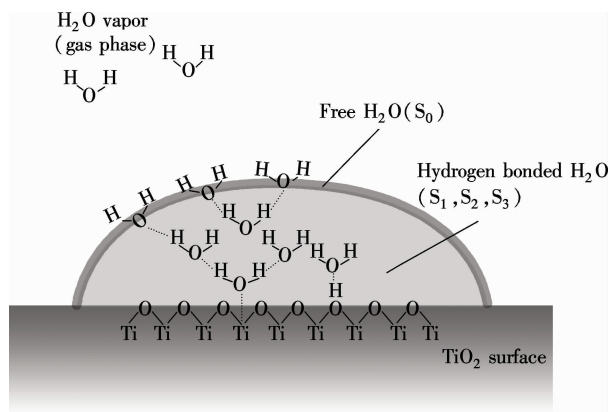


Fig. 8 Structural model of H_2O cluster adsorbed on solid surface of TiO_2 ^[13]

tilayers of H_2O contain plenty of ions forming new active sites for CO_2 absorption. The reaction rate is improved, and hence the CO_2 uptake in the first 10 min of carbonation is increased. After that, the reaction rate is controlled by the diffusion of CO_2 in the sorbent. So the rate is close to that of Sorb 1.

4 Conclusion

CO_2 capture/desorption behaviors of $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ doped with TiO_2 were researched in a bubbling fluidized-bed reactor. The effect of TiO_2 on carbonation is significant. $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ with around 1% TiO_2 loading exhibits a high CO_2 capture rate, particularly in the first 10 min. It is also indicated that TiO_2 is stable within the temperature range of the process. The sorbent structures of Sorb 1 and Sorb 2, including the surface area, the pore volume, and the pore size distribution, keep stable in 14 cycles. Furthermore, the impacts of flue gas constituents on TiO_2 doped $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ sorbents should be investigated in the future. We believe that this interesting research is promising for the use of dry sodium-based sorbents for CO_2 removal.

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TiO₂ 掺杂 Na₂CO₃/Al₂O₃ 吸收剂在流化床中的 CO₂ 捕集特性

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摘要: 由于 Na₂CO₃/Al₂O₃ 吸收剂的活性成分 Na₂CO₃ 与 CO₂ 反应活性较低, 选用 TiO₂ 作为掺杂剂, 采用浸渍法将其添加到 Na₂CO₃/Al₂O₃ 吸收剂中进行改性, 研制一种新型具有高反应活性的钠基固体吸收剂. 利用小型流化床反应器进行了 14 次循环脱碳/再生试验, 并对吸收剂进行了 XRD 和氮吸附表征. 结果表明: 掺杂 TiO₂ 后, 吸收剂与 CO₂ 的反应速率加快, 特别是在碳酸化反应的前 10 min 内; 反应前后除 TiO₂ 外无其他含 Ti 化合物生成; 碳酸化反应产物为 NaHCO₃ 和 Na₅H₃(CO₃)₄; 14 次循环反应后吸收剂仍保持稳定的微观结构. 采用 XPS 和 FTIR 分析了 TiO₂ 对 Na₂CO₃/Al₂O₃ 吸收剂脱碳特性的改性机理.

关键词: CO₂ 捕集; Na₂CO₃/Al₂O₃; TiO₂; 流化床试验

中图分类号: TK09