

Experimental Research on Flue Gas Desulfurization by Superfine Titanium Dioxide*

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Abstract: The mechanism of all present adopted desulfurization technologies is chemical reaction. A new kind of desulfurization medium — TiO_2 particle having large fraction void and specific surface area which is made from TiO_2 with superfine size sintered at low temperature and processed with surface activation is tested and investigated. The mechanism of desulfurization is mainly physical adsorption instead of traditional chemical reaction. Four samples of such TiO_2 particles were characterized by advanced instruments and tested for adsorption dynamics at the temperature range of 90 °C to 240 °C in a fixed bed. The results show that its adsorption ability for SO_2 in flue gas is dependent strongly on three factors: quality of TiO_2 particles, adsorption temperature and SO_2 concentration in flue gas. Titanium dioxide has well desulfurization character and pretty good prospect in engineering application. Sintered at temperature range from 440 °C to 540 °C, it has the best adsorption ability. In practical use the best adsorption temperature is around 120 °C.

Key words: FGD, titanium dioxide, sol-gel, physical adsorption, fixed-bed

Coal is the main energy resource (> 70%) in China and more than 80% of its annual production are burnt directly. The greenhouse effect, acid rain and the damage of ozone layer caused by dust, SO_2 and NO_x etc. in coal combustion products (flue gas) have become a serious problem of universal concern which will greatly influence the existence environment of mankind. Flue gas desulfurization (FGD) aimed for reducing SO_2 is one of the measures to solve this problem.

In traditional FGD processes such as limestone/gypsum scrubbing, LIFAC (limestone injection into the furnace and activation of non-reacted calcium) process and spray drier process, SO_2 is reacted with calcium-based sorbent chemically in the absorber and its reaction products should be treated properly before utilization. All the sorbents used in these processes is nonrenewable, that means the consumption of sorbents must be a large quantity for FGD process. Different from nonrenewable sorbents, renewable sorbents can be reused by regenerating after removing SO_2 . During regeneration process, element sulfur, sulfuric acid and some other useful industrial materials can be recovered. One of a few renewable sorbents is activated carbon, which is expensive and has heavy loss during regenerating, so it is not put in

industrial use until now. Some metal oxides such as CuO and ZnO can also be used as renewable sorbents. But it is costly for regenerating too. So, finding a cheaper renewable sorbent to meet the needs of industrial scale FGD is a very urgent task.

Titanium dioxide has been well known as a photocatalyst. When TiO_2 is excited by UV illumination, electrons and hole pairs will be generated in it and they reduce and oxidize absorbing rates on the surface, respectively with producing active oxygen such as OH radicals or super-oxide ions. Many researches have been conducted to apply this strong oxidation power for air cleaning or water purification. However, there have been little successful commercial products so far^[1]. We have tried to develop the novel application of TiO_2 for flue gas desulfurization (FGD) by physical and chemical adsorption and have got primary good results and innovation patent in China. In our investigation, we find that the adsorption property and renewable property of TiO_2 sorbent are both rather good. The removal SO_2 mechanism by TiO_2 particle is mainly physical adsorption instead of traditional chemical absorption. The preliminary experiments by using pigment-grade TiO_2 sorbent for flue gas desulfurization are carried out in a fixed bed reactor to investigate its possibility of prospect for industrial use. This article

presents titanium dioxide as a desulfurization sorbent and obtains some good experimental data. Superfine TiO_2 particle is prepared by sol-gel method, then sintered at low temperature and have its surface activated to get 1 mm – 2 mm TiO_2 sorbent particle with large fraction void and high specific surface area. The properties of this material for FGD are tested at the temperature range of 90 °C – 240 °C. The results demonstrate that the adsorption properties and renewable characters of this kind of sorbents are good and it is a new way for FGD process both in theory and practice.

1 Experiments

1.1 Apparatus

The scheme of the experimental apparatus is shown in Fig.1. The test set consists of three main parts: the gas feeding section, the adsorption reactor and the gas composition analytical section. The gas consists of two components: 0.22% (by volume percentage) SO_2 and the rest of N_2 , whose flow rate is measured and controlled by a mass flow controller. There is a bypass duct for the gas directly entering the analytical section during startup period of tests.

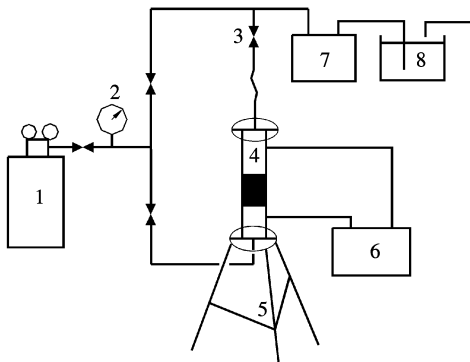


Fig. 1 The scheme of experimental set-up
1. Gas resource; 2. Flow meter; 3. Valve; 4. Fixed bed; 5. Support;
6. Temperature controller; 7. Gas analyzer; 8. Absorption solution

The reactor consists of three tubes made of stainless steel that prove to have sufficient corrosion resistance for various gas composition and different test conditions. One is outer tube with I.D. 16 mm and height 600 mm serving as preheating and shell of the fixed-bed reactor. Two are inside removable joint tubes with I.D. 10 mm and 12 mm, height 200 mm and 450 mm respectively for placing sorbents. Above parts are situated in an electric tube furnace. The temperature within the fixed bed is measured by a thermocouple and its temperature can be controlled between 50 °C and 800 °C.

The analytical section consists of a “ROSEMOUNT NGA 2000” gas analysis instrument (GAI) and a titration vessel fill with aqueous solution of sodium hydroxide. Sulfur dioxide via the reactor is selectively absorbed by TiO_2 sorbents in the reactor, and its concentrations at inlet and outlet of the test set are measured by a gas analysis instrument. The remained SO_2 from GAI is absorbed by aqueous solution of sodium hydroxide. The consumption rate of NaOH is proportional to the amount of sulfur dioxide leaving the reactor.

1.2 Sorbent materials

There are two steps to prepare the sorbent materials.

Firstly, prepare TiO_2 even disperse colloid. Take pigment-grade powder of TiO_2 and some stable reagent (i.e. polyethylene alcohol) into isopropyl alcohol solution inclusive phthalic acid four-ethyl ester, and add water to hydrolyze, then get stable colloid system of TiO_2 . In the process, control concentration of stable reagent and isopropyl alcohol and adding sequence and speed, the suitable size of TiO_2 particles and stability of colloid can be obtained.

Secondly, sintering the above materials at low temperature is to get high porosity rate, high specific surface area TiO_2 particles like sponge, then activating its surface in order to change surface physical and chemical properties. Under four different temperature, such as 340, 440, 540, 640 °C, 20 g sorbents for each are prepared respectively. These four TiO_2 sorbents are used in the experiments. All are prepared by a sol-gel technique with different content, pore size distribution and thermal history.

The basic characteristics of the sorbents used are summarized in Tab.1. On the basis of porosimetry and

Tab.1 Characteristics of sol-gel sorbents			
Sorbent	Particle size/mm	Apparent density/ ($\text{kg} \cdot \text{m}^{-3}$)	Specific surface area * /($\text{m}^2 \cdot \text{g}^{-1}$)
SG340	0.8 – 1.6	$\approx 1\,350$	63
SG440	0.8 – 1.4	$\approx 1\,100$	72
SG540	0.8 – 1.4	$\approx 1\,080$	74
SG640	0.8 – 1.2	$\approx 1\,020$	52

* By Hg porosimetry.

X-ray diffractometry it shows that the size of the crystals in all four sorbents is very small, between 1 and 10 nm. During heating of the sorbent to 650 °C at 40 k/h, no changes are observed in crystallinity (crystal growth) or in phase composition (no further formation of phases). The major differences of above

four sorbents are in the content of pores in the range 20 – 500 nm.

1.3 Adsorption procedure

The adsorption experiments are performed respectively in the reactor described above. The weight of sorbent used in each experiment is about 7g^[2]. Firstly, sorbent about 7.4 cm^[3] height layer was placed on the fixed bed support. After stabilization of the desired temperature in the reactor, sorption is commenced.

The temperature within the reactor tube in the region 0 – 200 mm above the bed support is practically constant, so the experiments can be considered to have been conducted under practically isothermal conditions. The linear superficial gas velocity ranges from 0.20 to 0.40 m/s^[5] depending on the temperature.

- The experimental contents are as follows:
- 1) Adsorption tests of four kinds sorbents (SG340, SG440, SG540 and SG640) at the inlet SO₂ concentration of 0.25%, and the inlet gas velocity of 0.22 m/s.
 - 2) Adsorption tests of SG540 sorbent under four temperatures of 120, 160, 200 and 240 °C.
 - 3) The influence of the inlet SO₂ concentration of 0.25% and 0.17% for SG540 sorbent.
 - 4) The influences of inlet gas velocities at 0.17 m/s and 0.23 m/s for SG540 sorbent.

Before each adsorption test, the SO₂ concentration in inlet gas should be measured. After each adsorption test, the SO₂ concentration in outlet gas should also be measured at regular intervals, such as thirty seconds or one minute or more long time, the adsorbed amount can be calculated by mathematical integral way.

2 Results and Discussion

- 1) Effect of sorbent properties
- Experimental data in terms of dependence of dimensionless SO₂ concentration at outlet on adsorption time are shown in Fig.2. Here, $\Delta C = C_{in} - C_{out}$, C_{out} and C_{in} represent SO₂ concentration in inlet gas and outlet gas of reactor respectively. From Fig.2 it can be seen that sorbents sintered under 440 and 540 °C have better adsorption properties, and the other two sorbents under 340 and 640 °C adsorption ability are lower. There are almost the same adsorption capacity for SG440 and SG540 in the same testing condition. Their adsorption quantity is shown in Tab.2. For one gram of SG540 sorbent can adsorb 29.6 mg SO₂ for SO₂

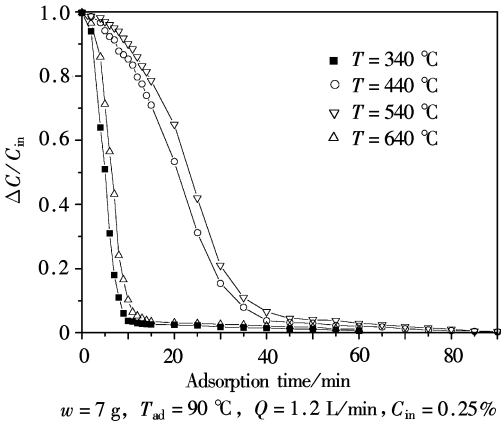


Fig.2 The relationships of sintering temperature and adsorption capacity

concentration of 0.22%. It has the highest adsorption capacity among above four sorbents. In order to investigate the desulfurization mechanism of TiO₂ particle deeply, above sorbents are analyzed by X-ray diffractometry (XRD). The XRD results show that these test samples are all anatase phase type, but their crystalline state is different. The 101 crystalline phase face diffractometry of SG440 and SG540 are stronger than the other two kinds, which show there are more abundant micro-pores of SG440 or SG540. So the sintering temperature is a very important factor for TiO₂ applied in FGD^[4].

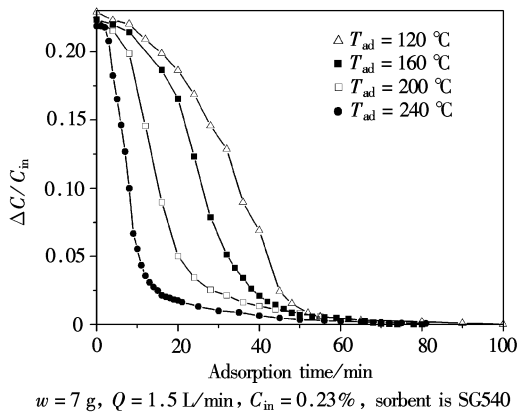
Tab.2 The adsorption capacities of TiO₂ sorbents in different sintering temperature

Sintering temperature/°C	340	440	540	640
Sorbents number	SG340	SG440	SG540	SG640
Adsorption capacity/(mg · g ⁻¹)	7.2	26.25	29.6	9.36

- 2) Effect of adsorption temperature in fixed bed
- The adsorption temperature in fixed bed is an important factor for sorbents sorption too. As shown in Fig.3, there are four experimental curves under temperature 120, 160, 200 and 240 °C, respectively. The inlet SO₂ concentration and inlet velocity of reactor are the same, and they equal to 0.23% and 0.22 m/s respectively. It can be seen that the best sorption case is at 120 °C, then is at 160, 200 and 240 °C in turn. With the adsorption temperature increasing, the quantity of adsorbed molecular may be flew off again, thus causing the adsorption efficiency decreased. But if the adsorption temperature is too low, the van der waals force is still strong enough that the sorption efficiency will also be reduced.

- 3) Effect of inlet SO₂ concentration

As shown in Fig.4, different inlet concentration of SO₂ has different adsorption efficiency in the same



$w = 7 \text{ g}$, $Q = 1.5 \text{ L/min}$, $C_{in} = 0.23\%$, sorbent is SG540

Fig.3 The relationships of adsorption temperature and adsorption properties

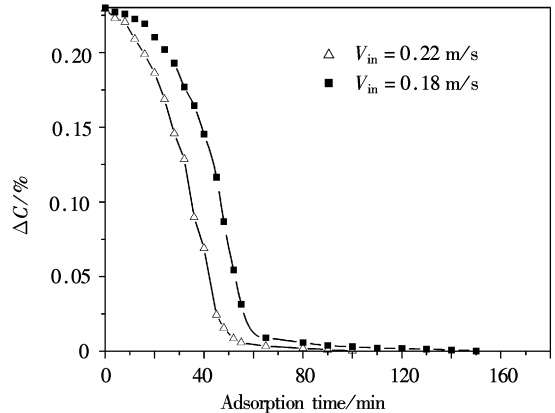


Fig.5 The relationships of adsorption time and adsorption capacity in different inlet velocity

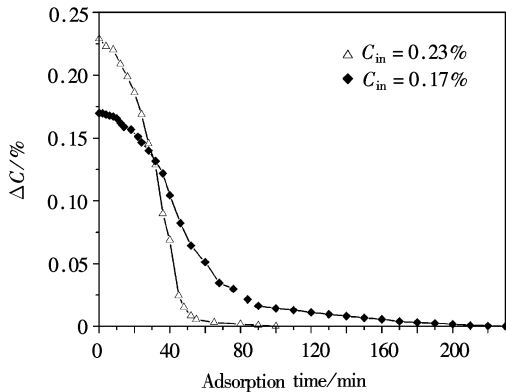


Fig.4 The relationships of adsorption time and adsorption capacity in different inlet concentration

adsorption time. With the inlet concentration increasing, TiO_2 sorbent adsorption efficiency is lower. But the amount of adsorption for both are almost the same. It is demonstrated if we let both adsorption time long enough, the adsorption capacity will tend towards accord.

4) Effect of inlet velocity of flue gas

As shown in Fig.5, the slower inlet velocity can get higher adsorption efficiency. Because slower inlet velocity can increase the residence time of the gas in fixed bed, SO_2 can fully contact with TiO_2 sorbent. In addition, slower inlet velocity can also decrease the amount of adsorbed SO_2 flying off.

3 Conclusions

1) Under low sintering temperature TiO_2 sorbents have better adsorption ability and good prospect in industrial application. The best sintering temperature for TiO_2 sorbent is between 440 and 540 °C, which influences the crystal state of TiO_2 sorbent and adsorption properties.

2) Adsorption temperature is an important factor for TiO_2 sorbent. The best adsorption temperature is

about 120 °C. With adsorption temperature increasing above 120 °C, the adsorption ability will be slow down.

3) With the inlet SO_2 concentration increasing, TiO_2 sorbent adsorption efficiency is lower in the same adsorption time. But if the adsorption time is long enough, the adsorption amount for different inlet SO_2 concentration will tend towards accord.

4) The lower the inlet velocity, the better the sorption efficiency is. But the lowest inlet velocity shouldn't be less than 0.17 m/s.

5) Titanium dioxide as a desulfurization sorbent is firstly presented to applied in FGD, and is shown pretty good practical prospect in industry.

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超细 TiO₂ 烟气脱硫的试验研究

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摘 要 目前烟气脱硫技术的反应原理多数为化学反应. 本文采用一种新型脱硫剂, 即用超细 TiO₂ 粉末经过低温烧结和表面活化制得的高孔隙率, 高比表面积的 TiO₂ 颗粒, 进行烟气脱硫的试验研究, 其脱硫机理主要是物理吸附. 在不同吸附温度下, 对 4 种 TiO₂ 颗粒吸附剂在固定床中进行了动态脱硫试验. 试验结果表明, 该吸附剂的脱硫能力主要与以下 3 个因素有关: TiO₂ 粒子的品质, 吸附温度以及烟气中 SO₂ 的浓度. TiO₂ 具有较好的吸附性能和工业应用前景. 烧结温度在 440~540 ℃ 之间时, 吸附剂的晶态形成有利于其吸附性能的提高, 试验最佳吸附温度为 120 ℃.

关键词 烟气脱硫, 二氧化钛, 溶胶-凝胶, 物理吸附, 固定床

中图分类号 TQ424.1