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# Design of Multi-Jet $H_2$/Air Flame Combustion Reactor and Morphology Control of $TiO_2$ Nanoparticles

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**Keywords:** Multi-jet, $H_2/O_2$ flame, Combustion reactor, $TIO_2$ nanoparticles

**Abstract:** Premixed multi-jet $H_2/O_2$ flame reactor was designed after analyzed the principle of $H_2/O_2$ flame reactor and disadvantages of tradition auxiliary reactor in this paper. Meantime, flame forms of premixed multi-jet $H_2/O_2$ flame reactor were observed by use of “empty model” experiment of heat fluid after combustion. Besides, qualitative discussion was carried out for influence of flame combustion form on temperature and concentration field of reaction zone. Finally, by use of multi-jet $H_2/O_2$ flame reactor and use $TiCl_4$ as precursor material, $TiO_2$ nanoparticles were prepared. It was high-temperature hydrolysis of gas phase by controlling process conditions such as $TiCl_4$ concentration, reaction temperature, $H_2$ flow of center loop and second loop. They had uniform particle size from 16 to 34 nm and rutile content 20%. Rutile content was controllable from 9 to 81%.

## 1. Introduction

$TiO_2$ possess many unique properties, such as good active catalyst, well permeability of visible light and strong absorption ultraviolet radiation etc. and have wide applications including catalysts, magnetic material, transducer, medicine and environment engineering, and others. It is an importance method to synthesize nanosized titanium particles by gas-phase combustion. The utilization of combustion flame synthesis has shown the promise of synthesizing nanoparticles in the desired size range with a uniform size distribution, high purity and fine industrialization.

Combustion reactor is the visual plant of synthesizing nanoparticles by gas-phase combustion, and the $H_2$/Air Flame Combustion Reactor is most wide application in the Combustion reactors. The morphology of nano-oxide not only turns on the chemical reaction and the dynamic of formation and growth, but also is enslaved to the flame structure and the engineering factor, such as the material flowing and mixing in the reactor, transfer of heat and quality etc. The design of combustion reactor becomes more complex because these processes are conjunct and influence each other, so many researchers are attracted to study the processes widely and deep. Furmenty developed counterflow diffusion flame reactor and synthesize nanosized $Al_2O_3$,$TiO_2$,$ZrO_2$,$GeO_2$ and others by $H_2$/Air Flame combustion in 1973.,Ulrich and Rishi synthesize nanosized $SiO_2$ by the turbulence-jet burning nozzle and premixed beehive $CH_4$/Air Flame Combustion reactor, such as the formation of flame, kinds of the nanosized particles and compound technology after 1994. Breiner and Duan xianjian developed free- jet flame reactor, which intensive mixing air, $H_2$ and $TiCl_4$ steam jet-flows into nozzle with high velocity and carry out the flame reaction in 2001. About all, Research on $H_2$/Air flame combustion reactor to synthesize nanosized particles has been intense in recent years. But the accordant view was not been reached to the detail pare, even the nucleus part of the $H_2$/Air flame combustion reactor because of the process of high temperature combustion and the complexity of the gas-phase reaction, and the reference to instruct how to design reactor is less.

Aiming at inner flames temperature and concentration gradient of existing combustion reactor being too great, which cause process having bad control on particle size and pattern, in-depth research on theory of multi-jet $H_2/O_2$ flame reactor, transfer behaviors and combustion reaction dynamics in combustion reaction process was conducted in this paper. We tried to develop multi-jet $H_2/O_2$ flame reactor with uniform concentration, temperature and residence time distribution properties. On this foundation, $TiO_2$ nanoparticles were prepared by combustion hydrolyzing premixed $H_2/O_2$ flame of $H_2$, air and $TiCl_4$. Moreover, influence of $TiCl_4$ star concentration, reaction temperature and reactor

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structure on crystal pattern, particle size and pattern of $TiO_2$ was studied systemically to get $TiO_2$ with controllable crystal form and particle size.

## 2. Reactor Design and Flame Formation

### 2.1 Reactor Theory and Structure

Favorable concentration, temperature and residence time distribution are requirement for synthesis of silica nanoparticles with uniform particle size distribution by use of $H_2/O_2$ flame reactor. Reactor designed must possess favorable concentration, temperature and residence time distribution which decided by the type and structure of reactors.

According to gas dynamics characteristic of coaxial multi-jet reported by document[1], multi-jet $H_2/O_2$ flame reactor was used for settling the combustion stability problem of premixed flame to improve uniform of concentration, temperature and residence time distribution in reaction zone further. The reactor was protected by annular auxiliary flame and air current which effectively decrease inspiration of free single jet and expand cord area range of potential flow. Because of “protect” of outer potential flow cord area for the inner and existence of auxiliary jet, coaxial multi-jet enlarged the length and range of potential flow cord area greatly and improved uniform of concentration, temperature and residence time further compare to free single jet[2]. Meantime, high gas rate of center reaction jet flow, ring type auxiliary flame and ring type air jet flow settled the problem of back fire of center tube and scar of jet flow nozzle, which made flame achieve safe and stable combustion.

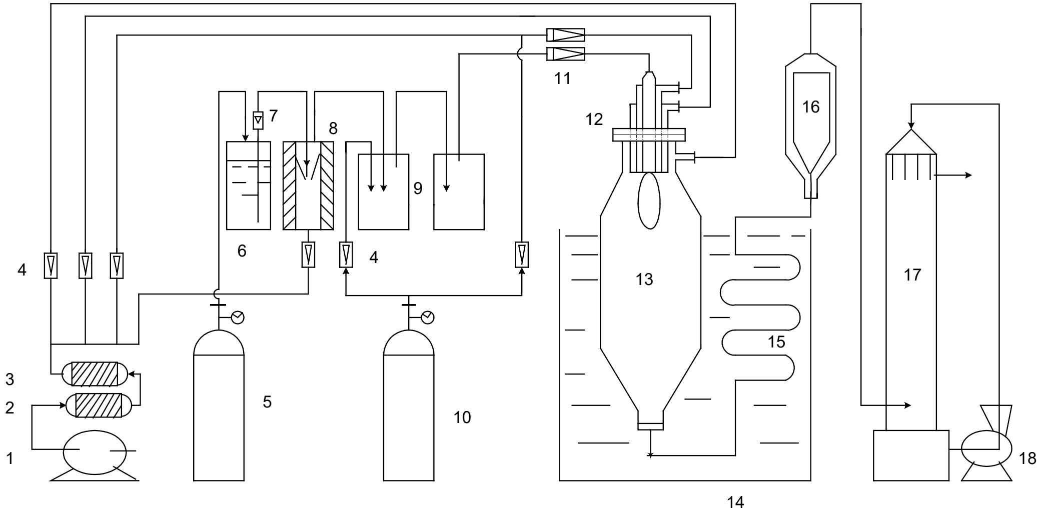
As above analysis of reactor theory, premixed multi-jet $H_2/O_2$ flame reactor designed by us consists of multi-jet nozzle, firebox and premixed container[3]. Multi-jet nozzle comprises center reaction tube, auxiliary ring, third ring and supplementary ring. 13 of Figure 1 shows reactor structure and gas trend of each ring. Air, $H_2$ and vaporization reaction material (take $TiCl_4$ for example) were put into mixer with proportion for intensive mixing and got into center tube of reactor nozzle with high gas rate to carry out combustion reactions; After mixed, the other air and $H_2$ jet flowed from auxiliary ring with slightly low gas rate to get auxiliary combustion, which expanded the range of potential flow kernel area and assured combustion stable; Two jet-flow air of third and auxiliary ring protected combustion reaction zone with lower gas rate which can further advance uniform of concentration, temperature and residence time and prepare nanoparticles with uniform crystal form, particle size and pattern distribution[4].

Considered heat-resisting property, anti-corrosive property, rigidity and working accuracy of equipment, material of jet-flow nozzle and firebox employ stainless steel. The following are principle geometric size and material of premixed multi-jet $H_2/O_2$ flame reactor:

## 3. Synthesis Flow and Conditions of Nanoparticles

### 3.1 Experimental Flow

Figure 1 shows the schematic of experimental apparatus for $TiO_2$ nanoparticle synthesis by $H_2$/Air Flames. Coming from compressor, air enters the bottom of $TiCl_4$ evaporator after dehydrated and dedusted and brings the $TiCl_4$ of pressed from reserve tank to first-level mixing container. At the same time, the $TiCl_4$ enters second-level mixing container after mixing with $H_2$ of coming from reserve tank. This intensive mixing air, $H_2$ and $TiCl_4$ steam jet-flows into center channel of reactor nozzle with high velocity and carry out the flame reaction; Mixed with $H_2$, the other flow of quantitative air pours into auxiliary ring of nozzle with rather low velocity and carry out auxiliary flame to ensure the center channel flame stable; the last two flows of jet-flows air enter tricycle and supplementary ring apart to protect the area of flame reaction which able to further improve the homogenization of reaction area’s temperature field, concentration field and residence time and then produce $TiO_2$ nanoparticle of crystal form, particle size and pattern distributing uniformly. Nanoparticles nucleate and grow up in firebox, coalesce and agglomerate in coagulator, is collected in particle collector. Reactor and coagulator are put into water bath and particle collector is heated with electric field to cool reactor and prevent condensate water separating out. Finally, HCl of off-gas is let out after disposed by HCl absorber.



(1. Air compressor; 2. Water extractor; 3. Air purifier;4 Gas flow indicator; 5. $N_2$ steel cylinder; 6. $TiCl_4$ reserve tank; 7. Liquid flow indicator; 8. $TiCl_4$ evaporator; 9. Mixing container; 10. $H_2$ steel cylinder 11. Fire arrestor; 12. multi-jet burner; 13. flame Reactor; 14. Water bath; 15. coagulator; 16. Particle collector; 17. HCl absorber; 18 recycle pump. )

Fig. 1 Schematic of experimental apparatus for $TiO_2$ nanoparticle synthesis by $H_2$/Air Flames

### 3.2 Experimental Conditions and Means

Various gas amount required by reaction is controlled with flowmeter; Demand temperature of reaction is regulated by controlling H2 amount when O2 excessive; Demand TiCl4 feed concentration of reaction is adjusted firstly by liquid flowmeter and then make it controllable by vaporizating all the TiCl4 with pervaporator. Mixer and its tubing accessing to the nozzle are heated by electricity to keep them at 180-200°C. The temperature of water bath and particle collector is kept on 90°C to prevent TiCl4 steam condensating. Reaction systemic pressure less than 0.2Mpa to make material carried favorably.

In the experiment, ignited nozzle must be stable for 5 minutes and TiCl4 is fed to reactor for 15 minutes every time. TiO2 powder collected from filter bag is taken to test and characterize. Table 1 shows specific conditions of TiCl4 feed concentration and gas flow. TiO2 powder collected from filter bag is taken to test and characterize.

Table 1 Experimental Condition List

| No | $TiCl_4$ (ml/min) | Central tube $H_2$($m^3$/h) | Central tube Air($m^3$/h) | Second tube $H_2$($m^3$/h) | Second tube Air($m^3$/h) | Third tube Air($m^3$/h) | Forth inlet Air($m^3$/h) |
|---|---|---|---|---|---|---|---|
| A | * | 0.84 | 3.0 | 0.99 | 1.5 | 8 | 17.5 |
| B | 15 | * | 3.0 | 0.99 | 1.5 | 8 | 15 |
| C | 15 | 1.07 | 3.0 | * | 1.5 | 8 | 15 |
| D | 15 | 1.07 | 3.0 | 0.53 | 1.5 | * | * |
| E | 15 | 1.07 | * | 0 .53 | 1.5 | 8 | 15 |

## 4. Morphological Control of $Tio_2$ Nanoparticle

### 4.1 Influence of $H_2$ in Center ring on Crystal Form and Particle Size

As condition B of Table 1 showed, when the $H_2$ flow of center ring increase from 0.3 to 1.37 $m^3$/h, its theoretical temperature (calculated according to reaction adiabatic temperature rise) improve from 1100 to 2400K successively and rutile content reaches its maximum here (temperature at 1700-1800K) which similar to the research result of Kobata[5]. The reason is reaction always produce anatase-type molecular cluster in the beginning and then there is two possibilities: one is particles continue growing into anatase-type crystal; the other is particles phase shift into rutile-type. Phase-shift rate is higher than anatase-type growth rate in the condition that temperature is lower than the maximum. At the same time, rutile particle content improves as temperature increase which leads to rutile content increases from 26% to 41%. When temperature reaches the maximum, increasing temperature decreases phase flaw concentration sharp and conversion rate of crystal form bring down greatly. Accordingly, rutile content of particles decreases to 28% as temperature increase. As $H_2$ flow of center ring increases from 0.3 to 1.37 $m^3/h$, specific area of product particles declines from 81 to 54 $m^2/g$ and the equivalent particle size calculated from these increases from 17 nm to 26 nm which showed as Table 1.

### 4.2 Influence of Second-ring $H_2$

Other process parameters are controlled as condition C of Table 1. Second-ring $H_2$ flow increases from 0.53 to 1.52 $m^3/h$ and Figure 2 indicates the XRD of product particle. As second-ring $H_2$ flow augmented, intension of diffraction peak (2θ=25.26) corresponding to anatase-type reaction strengthens successively while intension ((2θ=27.48) corresponding to rutile-type reaction weakens in turn. As Figure 3 showed, rutile content declines as linear from 49% to 27%. Along with the augment of second-ring $H_2$ flow, second-ring flame rate increases and its effect on center ring gets stronger which makes temperature of center ring getting higher. In this moment, center ring has been in high-temperature zone and rutile content of particles declines with temperature increases which according with temperature effect of center ring.

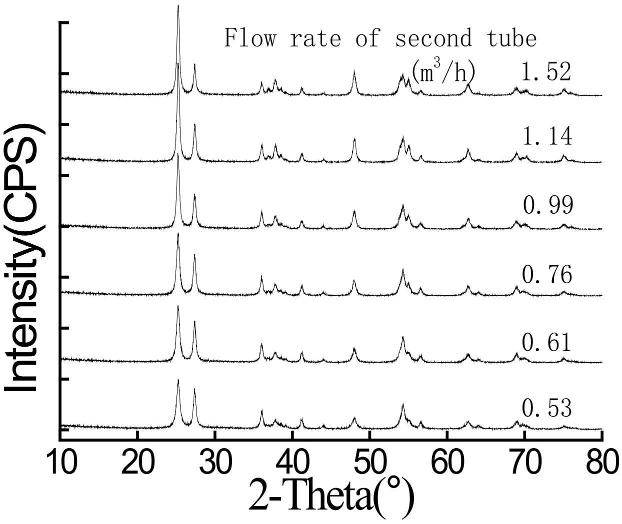


Fig.2 Xrd Patterns of $TiO_2$ Particles Synthesized

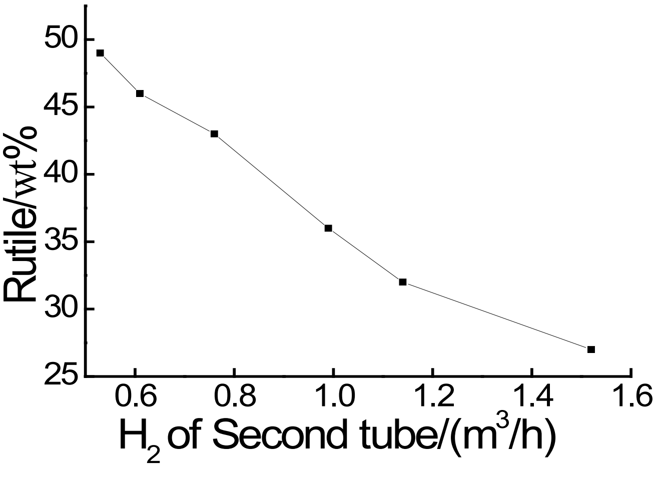


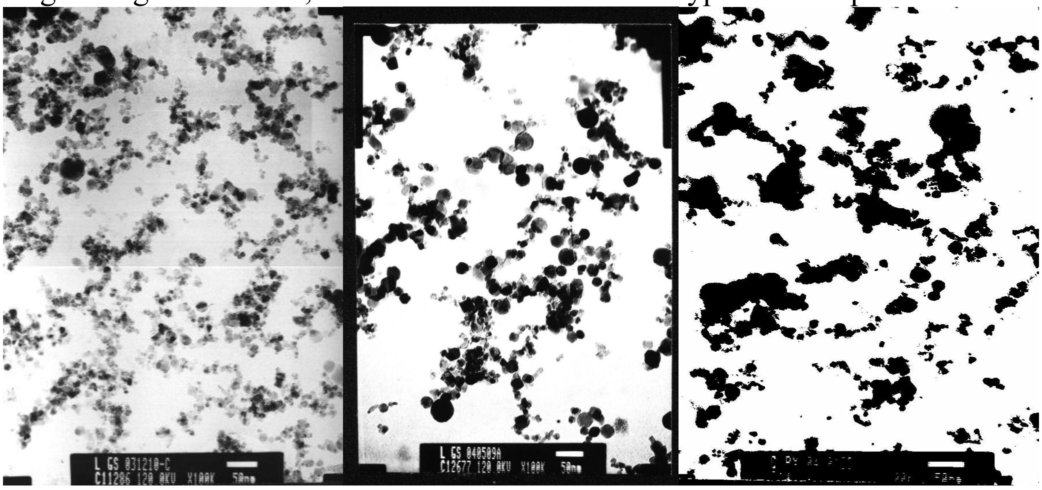
Fig.3 Effect of Flow Rate of Second Tube on

### 4.3 Influence of Reactor Structure on Crystal Form and Particle Size

Corresponding with condition D of Table 1, rutile content increases from 49%to 58% when third-ring and fourth-ring flow decreases from 8 and 15 $m^3/h$ to 3 and 5 $m^3/h$ respectively. Decrease of third-ring and fourth-ring flow directly affects gas velocity of flame room and makes it declines from 4.52 to 2.20 m/s, which causes residence time of primary particles in reactor double and accelerate anatase-type $TiO_4$ conversion into rutile-type and increases rutile content as a result. Center ring and second ring air in operational parameters has little influence on particle rutile content and this probably relates with inert gas $N_2$ of air. With air flow increase, $N_2$ dilution effect on concentration of reaction zone probably counteracts temperature effect which causes product particle size and rutile content have no change. Corresponding with condition E of Table 1, rutile content is 43, 41 and 46% when center ring flow is 1, 2 and 4 $m^3/h$ respectively. However, it can be expected to prepare $TiO_4$ particles fitting to be applied in different fields.

### 4.4 Influence of Flame Combustion Form on Particle Pattern

In the above, more uniform nanoparticle had been prepared with premixed flame according to reactor structure and flame combustion form. From discussion mentioned above, it can be concluded that $TiCl_4$ fed concentration cannot be high and temperature must be controlled to get $TiO_2$ nanoparticle with small particle size and 20% rutile content. Therefore, $TiCl_4$ fed flow is all chosen 10 ml/min. a, b of Figure 4 represents TEM of nanoparticle prepared from premixed flame. $H_2$ flow of center tube is 0.3, 1.37 l/h respectively and other conditions show as B of Table 1; c of Figure 4 indicates TEM of nanoparticle prepared from diffusion flame. Only air and $TiCl_4$ get into center tube, $H_2$ comes into second ring and has the same amount as that of b. Other conditions just the same as that of a and b. Showed as Figure 4, particle size of nanoparticles prepared from premixed flame is more uniform than that of diffusion flame general. With center tube $H_2$ flow of premixed flame increase, particle size gets large. Moreover, rutile content of these three types of nanoparticles is about 20%.



a b c

a-0.3; b-1.37; c-0+(1.37+0.99)

Fig.4 Tem Photographs of Particles Synthesized At Different Condition

## 5. Conclusion

Premixed multi-jet $H_2/O_2$ flame reactor was designed after analyzed the principle of $H_2/O_2$ flame reactor and disadvantages of tradition auxiliary reactor. Its structure and function were also expounded; Flame forms of premixed multi-jet $H_2/O_2$ flame reactor were observed by use of “empty model” experiment of heat fluid after combustion. Besides, qualitative discussion was carried out for influence of flame combustion form on temperature and concentration field of reaction zone. Compare to diffusion flame, premixed flame can provide more uniform temperature and concentration field; By use of multi-jet $H_2/O_2$ flame reactor and use $TiCl_4$ as precursor material, $TiO_2$ nanoparticles were prepared. It was high-temperature hydrolysis of gas phase by controlling reaction conditions. $TiO_2$ nanoparticles had uniform particle size from 16 to 34 nm and rutile content 20%. Rutile content was controllable from 9 to 81%; When $H_2$ and air of center ring had certain proportion, particle size and rutile content of product $TiO_2$ nanoparticles increased as $TiCl_4$ content and temperature increasing. Rutile content had maximum as temperature increased to certain value. In high-temperature zone, rutile content had linear decline as $H_2$ flow of second ring increasing; change of air flow had little influence on product crystal form while could improve particle uniform.

## Acknowledgments

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## References

[1] Formenti M, Juillet F, Meriaudeau P, et al. Preparation in a hydrogen-oxygen flame of ultrafine metal oxide particles. Oxidative properties toward hydrocarbons in the presence of ultraviolet radiation[J]. Journal of colloid and interface science, 1972, 39(1): 79-89.

[2] Akhtar M K, Vemury S, Pratsinis S E. Competition between TiCl4 hydrolysis and oxidation and its effect on product TiO2 powder[J]. AIChE journal, 1994, 40(7): 1183-1192.

[3] SHI L Y, LI C Z, ZHU Y H. TiCl4 Study on synthesis of nano-titanium dioxide particles by high-temperature vapor phase oxidation I. Particle size control[J]. Journal of Functional Materials, 2000(06): 622-624.

[4] JANG H D, Kim S K. Controlled synthesis of titanium dioxide nanoparticles in a modified diffusion flame reactor[J]. Materials research bulletin, 2001, 36(3-4): 627-637.

[5] GAO L, ZHENG S, ZHANG Q H. Nano-titanium oxide photocatalytic materials and applications M|. Beijing: Chemical Industry Press. 2002.