Progress of studies on preparation of TiO2 photocatalysts with sol-gel auto igniting synthesis

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Abstract: In this article, influencing factors on the kinetics of the process of Sol-gel Auto igniting Synthesis (SAS) which is an advanced technology for preparing nanometer particles of inorganic materials were reviewed. The studies on preparing of nanometer TiO2 photocatalysts with SAS were focused. It was concluded that SAS will play an important role in practical preparing of high-pure nanometer TiO2 powder, and as a technical support, preparation of titania TiO2 from titanic iron ore with SAS is feasible and practicable.

1 Introduction
Sol-gel Auto-igniting Synthesis, SAS, also called Low-temperature Combustion Synthesis, LCS, is a combustion synthesis using organics as reactant, developed in the 1990s [4]. A strong redox reaction will occur while organic salt gel or organic salt heated together with metal nitrate gel, and release huge heat which can maintain the reaction by itself. In the meantime, mass gas will be produced which can loosen the oxide powder. This combustion reaction is characterized by a lower igniting temperature (300~500℃), then making use of the combustion exothermic to reach the desired temperature of the reaction, and producing gas to prevent the powder to agglomerate and grow, to synthesize powders with uniform particles and high specific surface area. For this method occurred an extremely violent redox reaction in a very short of time, so it can be used to synthesize ultrafine particle with high temperature solid phase reaction at lower temperature. With SAS, some disadvantages in sol-gel process can be overcome such as high energy consumption, larger particles sintering in the synthesis of semiconductor photocatalysts by high temperature solid phase reaction. Now, there are some researches using this method for preparation of nanometer barium titanate powders, PSZ ceramic micro powders etc [1-4]. But there are still rarely researches or reports for the preparation of nanometer titanium dioxide photocatalysts [5-8].

In combustion synthesis, the type of fuel and composition influence the extent of the combustion reaction and phase formation. If the precursor solution only used nitrate without fuel, it does not burn during the heating process. The extent of the combustion reaction depends on the type of fuel or complexing agents, dosage and the ratio of fuel and nitrate in precursor. Meanwhile, controlling of the quantities of released gases in the reaction is one of the methods to adjust the powders’ performance [9-13].
2 Preparation of TiO$_2$ with SAS

In order to investigate the effects of pH value and water content on the photocatalytic activity of TiO$_2$ prepared by sol-gel auto-igniting synthesis (SAS) method, TiO$_2$ powders were prepared by changing pH value and water content, while using TiO(NO$_3$)$_2$ prepared by the TiCl$_4$ as precursor, and fixing the ratio of n(TiCl$_4$):n(C$_6$H$_8$O$_7$):n(NH$_4$NO$_3$)=1:1:3, the sintering temperature was 550$^\circ$C. The results showed as Figure 1 that the photodegradation rates constant gave the highest values with TiO$_2$ powders prepared with pH value of 7 and water mass fraction of 50%. The powders showed as excellent loose and porous materials. Also, a Fe$^{3+}$-doped nanosized TiO$_2$ photocatalyst was synthesized from a sol-gel based self-propagating high-temperature synthesis process (SHS) with TiCl$_4$ as the raw material. Its photocatalytic activity was studied by probing the degradation of methylene blue (MB) under different light irradiations including sunlight, low and high pressure mercury lamps. SEM results (Figure 2) indicate that the as-prepared nanoscale TiO$_2$ powder is a porous anatase material after SHS at 350$^\circ$C and heat-treatment at 500$^\circ$C. The optimal precursor molar ratio of n(Ti):n(citric acid):n(NH$_4$NO$_3$) is 1:3:5, the particle size is not bigger than 20 nm. Experimental results show as Figure 3 that the highest photocatalytic activity of Fe$^{3+}$-doped TiO$_2$ could be achieved when the molar ratio of Fe$^{3+}$ to TiO$_2$ is 0.02%. Removing rate of MB was 96.1% with Fe$^{3+}$-doped TiO$_2$ as catalyst and sunlight as light source, which is 1.78 times of that of pure TiO$_2$. Furthermore, to study the effect of different incendiary agent loading on photocatalytic activity of TiO$_2$, TiO$_2$ powders were prepared with sol-gel auto-igniting synthesis (SAS) method, while tetra-n-butyl titanate and TiCl$_4$ were used as precursor separately. The structure of TiO$_2$ was characterized with XRD and SEM, and photocatalytic activity examined with degradation of methylene blue (MB). Results showed as Table 1 indicated that TiO$_2$ powders shows as excellent loose and multi-hole material prepared with SAS. With tetra-n-butyl titanate and TiCl$_4$ as precursor, the optimal ratio of n(Ti):n(citric acid):n(NH$_4$NO$_3$) are 1:1:2 and 1:3:5, the according particle sizes are 0.1μm and 20nm, degradation rate constants of MB increase 60% and 100% compared with normal TiO$_2$ powder prepared without SAS method.

![Fig.1 Degradation of MB with TiO$_2$ prepared with different pH value and water content.](image1)

![Fig.2 SEM pattern of TiO$_2$ powder.](image2)

![Fig.3 Degradation of MB with different light source.](image3)
Tab.1 Photodegradation rate constant \( k \) of MB with different TiO\(_2\) as catalyst.

| No. | precursor | n Ti | n citric acid | n NH\(_4\)NO\(_3\) | k (min\(^{-1}\)) |
|-----|-----------|------|---------------|---------------------|-----------------|
| a   | tetra-n-butyl titanate | 1    | 0             | 0                  | 0.014           |
| b   | tetra-n-butyl titanate | 1    | 0.5           | 0                  | 0.017           |
| c   | tetra-n-butyl titanate | 1    | 0.5           | 1                  | 0.018           |
| d   | TiCl\(_4\)    | 1    | 1             | 1                  | 0.021           |
| e   | TiCl\(_4\)    | 1    | 1             | 2                  | 0.023           |
| f   | TiCl\(_4\)    | 1    | 2             | 2                  | 0.023           |

A

| No. | precursor | n Ti | n citric acid | n NH\(_4\)NO\(_3\) | k (min\(^{-1}\)) |
|-----|-----------|------|---------------|---------------------|-----------------|
| A   | TiCl\(_4\)    | 1    | 0             | 0                  | 0.014           |
| B   | TiCl\(_4\)    | 1    | 2             | 3                  | 0.020           |
| C   | TiCl\(_4\)    | 1    | 2             | 4                  | 0.023           |
| D   | TiCl\(_4\)    | 1    | 3             | 5                  | 0.028           |
| E   | TiCl\(_4\)    | 1    | 3             | 6                  | 0.028           |

Obviously, there are many factors influencing SAS. It can be considered that preparation of TiO\(_2\) photocatalysts with SAS have not been studied deeply and reported enough. So, it is necessary to study every effecting factor systematically and deeply.

3 Conclusions
SAS has increasingly attracted the attention of material scientists by its unique advantages. Although SAS has also disadvantage of higher cost of raw materials compared with the solid phase reaction, hydrothermal synthesis method and other processes, its attractions include simple synthetic process and simple equipment and so on, the most important is that multi-component compound is easy to synthesize and the nanoscale products have excellent properties. Therefore, SAS has good prospects in terms of some multi-component materials which were difficult to synthesize by the traditional methods. The metal ion is soluble or can be complexed in SAS process easier. However, because of the diversity of the system, some metal ions are insoluble or hard to combine with complexing agents, part of iron metals can easily precipitate in the water evaporation process. It still requires more studies on these problems for SAS can be applied successfully in the preparation of TiO\(_2\). To control the particle size and decrease powder agglomeration in combustion synthesis are also the important goals of further studies.

In a word, the sol-gel auto igniting synthesis process has good prospects in the application for preparation of high purity nanometer TiO\(_2\).

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