Nature of Invention: Chemical molecule and synthesis route

Applicant: SynergyX

Inventors: Mitesh Wandhare, Satvik Pratap Singh

Chemical Formula: TiO_2

Chemical Name: Titanium Dioxide

Chemical synthesis routes:

a. LAB SCALE SYNTHESIS:

Sol-Gel Method:

1. Raw Materials:

- Titanium(IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$)
- Acetic acid (CH_3COOH)
- Ammonium hydroxide (NH_4OH)
- Nitric acid (HNO_3)
- Citric acid monohydrate ($(C_3H_5O(COO)_3)H_3.H_2O$)

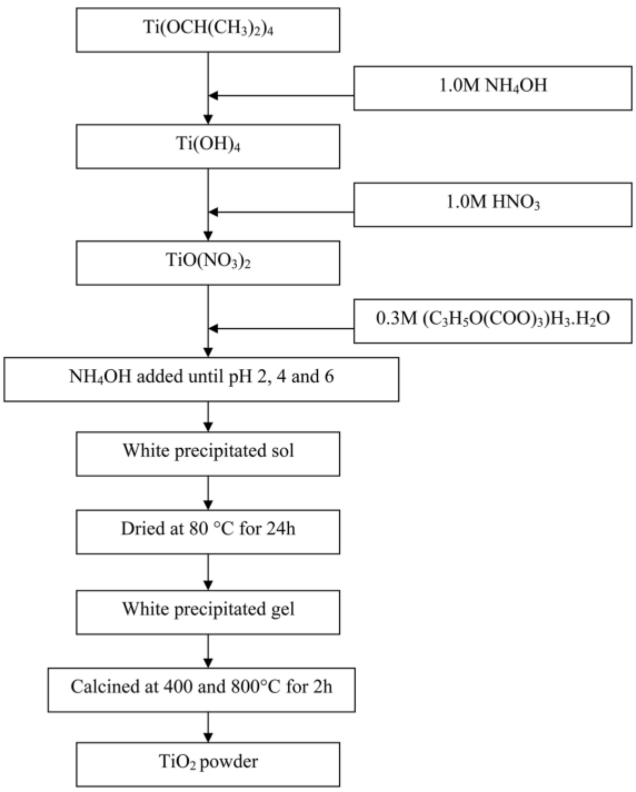

Fig. 1. Schematic diagram for the synthesis of TiO_2 powder by a sol-gel method.

2. Reaction Steps:

Titanium dioxide (TiO2) powder was prepared by a sol-gel method as shown in Fig. 1 Titanium isopropoxide. [$Ti(OCH(CH_3)_2)_4$] (97% Aldrich, England), ammonium hydroxide (NH_4OH) (30% BDH, England), nitric acid [HNO_3] (65% Merck, Germany) and citric acid monohydrate [$((C_3H_5O(COO)_3)H_3.H_2O)$] (99% Ajax, Australia) were used as the starting materials.

1. **Preparation of Titanyl Nitrate:**

- 1.0 M NH_4OH solution was added to Titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$] in an ice bath at 10 ℃ to form titanic acid [$Ti(OH)_4$]
- Titanyl nitrate ($TiO(NO_3)_2$) is then formed by dissolving titanic acid with 1.0M nitric acid (HNO_3)

Reaction:

$$Ti(OCH(CH_3)_2)_4 + 4\,NH_4OH \rightarrow Ti(OH)_4 + 4(CH_3)_2CHOH + NH_4NO_3$$

$$Ti(OH)_4 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 4H_2O$$

2. **Formation of Sol:**

- Deionized water containing 0.3 M [$((C_3H_5O(COO)_3)H_3.H_2O)$] and 1.0 M NH_4OH were added to adjust the pH value of the solutions. The white precipitated sol was obtained after adjusting the final range of pH of the solution to 2-6.
- The sol is formed as a white precipitate.

Reaction:

$$TiO(NO_3)_2 + 2(C_3H_5O(COO)_3)H_3 + \ 4\,NH_4OH \rightarrow Ti(C_3H_5O(COO)_3)_2 + 2NH_4NO_3 + 4H_2O$$

3. **Co-Precipitation:**

- The sol undergoes co-precipitation at pH values ranging from 2 to 6.
- Adjusting the final pH of the solution results in the formation of co-precipitated powder.

4. **Washing and Drying:**

- The co-precipitated powder is washed to remove any impurities.
- It is then filtered and dried in an oven at 80°C for 24 hours.

5. **Calcination:**

- The dried gel undergoes calcination at temperatures of 400°C and 800°C for 2 hours.
- Calcination induces the crystallization and phase transformation of TiO_2.

Reaction:

$$Ti(C_3H_5O(COO)_3)_2 \rightarrow TiO_2 + CO_2 + H_2O$$

b) Other routes:

Hydrothermal Synthesis:

1. Raw Materials:

- Titanium(IV) sulfate $Ti(SO_4)_2$ or titanium(IV) isopropoxide $Ti(OC_3H_7)_4$
- Hydrochloric acid (HCl) or sulfuric acid (H_2SO_4)
- Distilled water (H_2O)

2. Reaction Steps:

a. Formation of Titanium Hydroxide Precursor:

- Titanium(IV) sulfate or titanium(IV) isopropoxide is dissolved in water.
- Diluted hydrochloric acid or sulfuric acid is added to the solution to hydrolyse the titanium precursor.
- The hydrolysis reaction can be represented as:

$$For\ Ti(SO_4)_2: Ti(SO_4)_2 + 2HCl + 4H_2O \rightarrow Ti(OH)_4 + 2H_2SO_4$$

$$For\ Ti(OC_3H_7)_4: \ Ti(OC_3H_7)_4 + 4H_2O + 4HCl \rightarrow Ti(OH)_4 + 4C_3H_8O$$

This step produces a titanium hydroxide precursor.

b. Conversion to Titanium Dioxide:

- The titanium hydroxide precursor is then heated to a moderate temperature (60-80°C) for several hours.
- This heating drives off water molecules, leading to the conversion of titanium hydroxide to titanium dioxide:

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$$

This step forms TiO_2 nanoparticles.

c. Crystallization of $\boldsymbol{TiO_2}$:

- The TiO_2 nanoparticles are subjected to a hydrothermal treatment at high temperature (100-200°C) and autogenous pressure.
- Under these conditions, the TiO_2 nanoparticles undergo nucleation and growth, leading to the crystallization of TiO_2.

This step is crucial for obtaining TiO_2 with desired crystalline structure and morphology.

3. Washing and Drying:

- After crystallization, the TiO_2 nanoparticles are washed with distilled water to remove any residual impurities or by-products.
- The washed TiO_2 nanoparticles are then dried at a moderate temperature to remove excess water and obtain the final product.

4. Conditions:

- High temperature (100-200°C) and autogenous pressure are maintained during the hydrothermal treatment to promote the crystallization of TiO_2.

5. Product Yield and Purity:

- The yield of TiO_2 nanoparticles typically depends on the reaction conditions and can range from 70% to 90%.
- The final purity of TiO_2 nanoparticles can be enhanced through multiple washing steps to remove residual impurities.

Precipitation Method:

1) **Raw Materials**:

- Titanium (IV) chloride (TiCl4)
- Ammonium hydroxide (NH4OH)
- Distilled water (H2O)

2) **Reaction Steps:**

1. **Preparation of $TiCl_4$ solution:**
    - We would start by preparing a TiCl4 solution by dissolving titanium (IV) chloride in distilled water.
    - The receiving water is maintained at 0°C while TiCl4 is added dropwise under vigorous stirring. The resulting precursor solution has a TiCl4: H2O volume ratio of 1:4.
2. **Mixing with NH4OH:**
    - Now we need to set up a reaction vessel equipped with a stirrer and a temperature control system. While stirring the TiCl4 solution, slowly add the ammonium hydroxide (NH4OH) solution dropwise to the reaction mixture.
    - Control the addition rate and monitor the pH of the solution continuously. Typically, the pH is adjusted to a specific range of around 7-8.
    - Maintaining the reaction temperature within a controlled range is crucial **(310-340K)** to optimize the reaction kinetics.
3. **Precipitation of TiO2:**
- On the addition of NH4OH, formation of a white precipitate is observed, indicating the formation of titanium dioxide (TiO2).
- Now need to allow the reaction to proceed until the precipitation is complete, typically indicated by the cessation of gas evolution and the settling of the precipitate.

- **The Reaction of Following Process is:**

$$\mathbf{TiCl_4 + 2NH_4OH \text{-----}\rightarrow TiO_2(s) + 4NH_4Cl + 2H_2O}$$

4. **Washing and Drying:**
    - Washing the precipitate is crucial to ensure purity of final product and need to remove any soluble impurities or by-products, such as ammonium chloride (NH4Cl), from the surface of the TiO2 particles.
    - After washing, the TiO2 precipitate is dried to remove excess water and obtain the final product in solid form.

Pechini Method

1. **Raw Materials:**
    - Titanium (IV) isopropoxide ($Ti(OC_3H_7)_4$)
    - Citric acid(C6H8O7)
    - Distilled water (H2O)
    - Ethylene Glycol
2. **Reaction Steps**:

    i. **Preparation of Polymeric Precursor:**
    - Firstly, need to Dissolve citric acid in distilled water to form a solution. The Concentration of citric acid may vary, but it's used to ensure complexation with the metal precursor.
    - Add titanium (IV) isopropoxide ($Ti(OC_3H_7)_4$) to the citric acid solution while stirring continuously to ensure homogeneity of the solution.
    - Now we slowly add ethylene glycol to the solution. Ethylene glycol serves as a cross-linking agent and helps in the formation of the polymeric network. And this involves formation of the polymeric precursor involves the chelation of citric acid with the titanium (IV) isopropoxide, leading to the formation of a stable complex.
    - The Reaction of following is:

$$\mathbf{Ti(OC3H7)4 + n\ Citic\ acid + m\ Ethylene\ glycol\ -\rightarrow Polymeric\ Precuursor}$$

    ii. **Polymerization:**
    - Initially heat the solution containing citric acid, $Ti(OC_3H_7)_4$, and ethylene glycol on a hot plate or in a water bath at a moderate temperature around (300-380K). This step promotes the polymerization reaction and the formation of a stable polymeric precursor.
    - We need to stir the solution continuously during polymerization to prevent the formation of gel-like aggregates.
    - The reaction involved in the following is:

$$\boldsymbol{Polymeric\ Precussor} \rightarrow \mathbf{TiO2(s)} + \boldsymbol{Volatile\ org\ compounds} + \boldsymbol{Carbonaceous\ residue}$$

    iii. **Heating and Calcination:**

- After polymerization, continue heating the solution, we need to remove excess water and organic components. This is carried out at temperature higher than B.P of water but lower than decomposition temperature of polymer.
- Once the organic components are removed, then further increase the temperature to initiate the decomposition and crystallization of the polymeric precursor to form TiO2.
- The process of Calcination is typically performed at higher temperatures. (**400-800°C**) in a controlled atmosphere of air or inert gas to promote crystallization, phase transformation, and the removal of residual carbonaceous species.
- The reaction involved in this is:

$$TiO2(Amorphous) — \textit{TiO2(crystalline)}$$

iv. **Characterization:**

- We finally need to Characterize the synthesized TiO2 product using analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), to evaluate its crystalline structure, morphology, surface area, and chemical composition.
- The Pechini method offers several advantages such as control over stoichiometry, homogeneity, and the ability to produce complex compositions.

References:

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2. Synthesis of TiO2 Nanoparticles by Hydrothermal Method and Characterization of their Antibacterial Activity: Investigation of the Impact of Magnetism on the Photocatalytic Properties of the Nanoparticles **.**

3. Effect of hydrolysis conditions on morphology and phase content in the crystalline TiO2 nanoparticles synthesized from aqueous TiCl4 solution by precipitation, Jeong Hoon Lee, Yeong Seok Yang

4. Pechini Processes: An Alternate Approach of the Sol–Gel Method, Preparation, Properties, and Applications
5.Hydrolysis of TiCl4 and Precipitate formation-ACS Publication.

List the contributions of each author:

1. **Mitesh Wandhare,220650:**

- Designed and implemented the sol-gel method for the synthesis of Titanium Dioxide (TiO2) powder.
- Selected appropriate raw materials, including Titanium isopropoxide, ammonium hydroxide, nitric acid, and citric acid monohydrate, considering their availability and suitability for the process.
- Investigated the effects of pH, temperature, and precursor concentrations on the synthesis process, leading to the identification of optimal reaction parameters.
- Played a role in evaluating alternative production processes, such as hydrothermal synthesis and precipitation method.

2.Satvik Pratap Singh,220981:

- Designed and implemented the precipitation and Pechini method for the synthesis of Titanium Dioxide (TiO2) powder.
- Chose the most suitable raw materials, Titanium isopropoxide, ammonium hydroxide, Ethylene glycol, and citric acid monohydrate, taking into account both their accessibility and compatibility with the intended process.
- Explored the impact of pH, temperature, and precursor concentrations on the synthesis process, culminating in the determination of the most favourable reaction conditions

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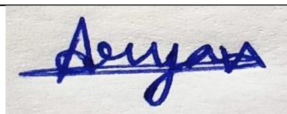
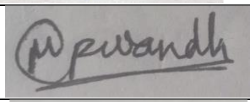
Aryan Nigam	220227	
Mitesh Wandhare	220650	
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