Using Waste SCR Catalysts to prepare nano TiO_2 photo catalyst and to degrade dye waste water

Abstract

In this study, TiO_2 contained in Waste SCR Catalysts is recycled using acid or alkaline. In the alkaline process, waste catalyst powder is reacted with NaOH under high temperature for frit reaction to form Na_2TiO_3. Na_2TiO_3 then reacts with HCL to get $TiCl_4$ solution. $TiCl_4$ solution is then added with sodium pyrophosphate to increase its dispersion characteristic, in the meantime, PS micro ball is polymerized as carrier. $TiCl_4$ solution is hydrolyzed to form TiO_2 to co-deposit onto PS micro ball. Powder is then cleaned and calcined. After removing PS micro ball, porous TiO_2 powder can then be obtained. In the acid process, sulfuric acid solution and waste catalyst were heated to form solid titanium oxysulfate. Titanium oxysulfate then hydrolyzes to form TiO_2 powder. Powder was then filtered, baked, grinded and calcined to form photo catalyst powder. The above two TiO_2 photo catalysts prepared from Waste SCR Catalysts with diameter 30-40 nm have photo catalyst characteristic and advantages.

Then nano TiO_2 photo catalysts obtained from two processes were tested and compared respectively. In the test, EDS and ICP were used to analyze the elemental composition of TiO_2, and XRD was used to analyze the crystalline phase. SEM and TEM were used to analyze the surface morphology, structure and particle size. Meanwhile, the suspension effect of porous TiO_2 was also tested. This study investigated the production of photo catalyst from SCR catalyst, and its effect in Advanced Oxidation Processes (AOP). Meanwhile, under the presence of UV/TiO_2, dye waste water was degraded, and TOC removal rate obtained was above 90%.

1 Foreword

SCR Catalysts was used in decomposing NOx contained in the air. It has wide application field, for example, chemcial plant, semiconductor plant, thermal power plant, boiler, heavy oil burner and diesel oil vehicle, etc. In other words, device that will generate waste gas of NOx compound needed to have SCR Catalysts installed at the exhuast part to prevent the release of NOx to the air. In the structure of Waste SCR Catalysts, V_2O_5 and MO_3 were used as the active component of the catalyst to be

depostied on TiO_2 carrier. The reason to use TiO_2 as carrier was because TiO_2 can resist very well the acid gas. In SCR Catalysts, the content of V_2O_5 and WO_3 was respectively 5-10%, and the rest was TiO_2 carrier. Since SCR Catalyst was used in waste gas of high temperature, V_2O_5 and WO_3 was gradually sintered with TiO_2 carrier, and the activity of catalyst got reduced gradually, therefore, change was the only way. For Waste SCR Catalysts, the present handling method was alkaline method, V_2O_5 and WO_3 in it was taken out, and the rest of TiO_2 carrier was abandoned, the disposal of TiO_2 could lead to environmental pollution and resource waste.

TiO_2 has many applications, for example, the dye in paint. Its seciond application was in electronic ceramic material application for manufacturing $BaTiO_3$, $SrTiO_3$ and Lead Zirconate Titanate. Third application is as the carrier of catalyst, in such application, its resistance to acid and alkaline and resistance to high temperature is used. The fourth application is as photo catalyst, and nano TiO_2 has a strange characteristic. Nano TiO_2, under the existence of sunshine, water and air, can decompose water into ·OH radical, and oxygen in the air can be turned into ·O2- radical. ·OH radical is a strong oxidizer, ·O2- radical can react with water and capture electron to become ·OH radical, and both of them are strong oxidizers and are able to decompose organic substance, they can change organic substance into CO_2.

In 2000, Zhong et al. [1] have used titanium isopropoxide as precursor to be added into cationpolystyrene micro ball to let hydrolyzed TiO_2 to cover onto PS micro ball. When the correlation between gel and solvent can be well controlled, then a homogeneous shell can be covered onto PS micro ball. When controlling the shell thickness, then dissolve or melt PS ball, TiO_2 hollow ball can be obtained. In 2003, Yang et al. [2] have used titanium(IV) tert-butoxide as precursor, and seed-emulsion polymerization has been used to prepare PS micro ball of particulate diameter of 275 nm. First, PS ball was immersed into concentrated sulfuric acid for sulfonation, PS ball after sulfonation was used as carrier and dispered into a mixture solution of titanium(IV) tert-butoxide and alcohol so that titanium(IV) tert-butoxide will be adsorbed onto PS ball, next, then it was centrifuged and dispersed into alcohol aqueous solution for reaction. Then PS/TO_2 shell structural particle was prepared, then through N,N-dimethylfomamide to dissolve PS and then through calcination, TiO_2 hollow micro ball was formed. In 1972, Japan’s Fujishima Akira and Dr. K.Honda [3] have used respectively photo catalyst semiconductor titanium oxide single crystalline and Pt as electrode to conduct water decomposition reaction. After it was illuminated by mercury lamp, bubbles will be generated on both electrodes. After collecting the gas for analysis, it was proved that gas generated on the titanium oxide single crystalline electrode was oxygen, and gas generated on the platinum electrode was hydrogen. Under the condition with only light illumination but without any

electric field applied, the use of titanium oxide can successfully decopose water into hydrogen and oxygen. The use of solar energy to prepare hydrogen has great meaning to relieve energy crisis, which cause immediately extensive attension in the academy. In 2002, Zhang and Gao [4] have used titanium propoxide as precursor. They used Span 80, water and toluene to form water/oil microemulsion, through the adjustment of proportion between water and Span 80, the particulate diameter of TiO_2 particles formed was controlled. In 2002, Jang and Lee [5] have used surfactant to let methanol form micelle to be dispersed in water, then mixed solution of isooctane and styrene was dropped into to prepare polystyrene hollow ball under a reaction at 70℃. In 1998, Kasuga et al. [6], under 110 ℃, have used 5 ~ 10 mol· L^{-1} NaOH solution to treat anatase TiO_2 powder, then through HCl acid treatment, TiO_2 nano piece was formed, then Ti-OH bond at the end interacted to form nano tube. In 2002, Stefanie and Maret[7] have used titanium ethoxide as precursor, then negative charge carrying PS micro ball was used as carrier, then the carrier was dispersed into absolute ethanol. Then add precursor quickly, then through electrostatic force and self-organization effect between precursor and carrier, it was allowed to absorb onto the surface of PS micro ball. Through the dissolution of PS by organic solvent, TiO_2 shell structural particle was formed, or through calcination, rutile phase TiO_2 hollow micro ball was formed. There were many ways to prepare TiO_2, but the one with more studies and more extensively used was Sol-Gel Method, Chemical Vapor Deposition (CVD), Liquid Phase Deposition (LPD) and precipitation method, etc. [12]. There were many ways to prepare polystyrene too, and more mature methods included Emulsion Polymerization, Emulsifier-free Emulsion Polymerization, Dispersion Polymerization and Suspension Polymerization [7] . Through the reuse of Waste SCR Catalysts to prepare nano TiO_2 photo catalyst was a novel chemical technology. It has great meaning for solving waste catalyst environment pollution and for turning waste into resource.