行政院國家科學委員會專題研究計畫成果報告

新型鈦氧化物之製備與鑑定

Synthesis and Characterization of Novel Titanium Oxide Compounds

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一、 中文摘要(關鍵字:鈦氧化物, 拉曼光譜)

鈦氧化物為去硝觸媒及光電材料的重要成份, 本計畫研究鈦氧化物之相關物之熱分解反應及水浴法反應, 仔細的鑑定各種溫度的分子種類及結構, 清楚的解析相關物質的鍵結形態, 配位行為及活性穩定性等重要性質. 充分掌握拉曼光譜及鈦氧化物之特性, 從而對重要之化合物合成, 結構及反應等加以研究, 突破其他鑑定技術之瓶頸.

二、 Abstract (Key Words: titanium oxide, Raman spectroscopy)

Synthesis and characterization of novel organic/inorganic titanium oxide compounds, prepared by hydrothermal synthesis, employing structure directing agent, is described. Under hydrothermal condition, the effects of titanium precursor, structure-directing agent, temperature, solvent, pH and reaction time on the synthesis of novel titanium oxide compounds have been examined by Raman spectroscopy as a major probe to obtain in-situ information of the conversion process.

三、 計畫緣由與目的

Among the published reports so far, synthesis of novel titanium oxide utilizing SDA under hydrothermal condition appears to be relatively unexplored. Few reports on the speciation of titanates either in aqueous solution or on various supports have been reported. Aqueous titan species such as $[Ti_8O_{12}(H_2O)_{24}]^{+8}$, $Ti(OH)_2^{+2}$, $Ti(OH)_3^{+1}$, TiO^{+2}, $Ti(OH)_6^{-2}$, are usually generated in delicate compositional condition; whereas TiO_2 films have been deposited on various substrates, such as self-assembled monolayers on Si, through CVD, MOCVD and sol-gel techniques. On the other hand, characterization of amorphous titanate species still remains a challenge which greatly hampers tailoring the desired properties of titanium oxide-related materials. However, types of hydrated forms of titanium oxide, usually reflecting the coordination flexibility of titanium oxide framework, have been reported to consist H_4TiO_4, $H_2Ti_2O_5$ and $H_2Ti_8O_{17}$. In comparison, distribution of silicate, vanadate, molybdate and tungstate species can be manipulated by highly controlling factors such as temperature, concentration, pH and starting materials; whereas numerous organic/inorganic hybrid compounds have been reported. Thus, in order to synthesize novel organic/inorganic hybrid titanium oxide compounds, a better capability to characterize and manipulate titanate species in aqueous solution appears to be critical. Characterization of catalytic materials has for a long time paid insufficient attention to solids of non-periodic structures, which were considered as background because of its higher complexity. However, their importance is by no means ignored, which creates a need for correlating their synthetic properties with highly differentiated structures and bonds. Thus, in order to synthesize novel organic/inorganic hybrid titanium oxide compounds, a better capability to characterize and manipulate titanate species in aqueous solution appears to be critical. Characterization of catalytic materials has for a long time paid insufficient attention to solids of non-periodic structures, which were considered as background because of its higher complexity. However, their importance is by no means ignored, which creates a need for correlating their synthetic properties with highly differentiated structures and bonds. For examples, recent efforts in synthesizing advanced catalytic materials have focused on utilizing molecular precursors to ensure homogeniety of conversion process which exhibit transitional amorphous structures during the evolution toward final crystal. Previous work in synthesis of mordenite, zeolite Y, layered materials and barium titanate have concluded that characterization and control of these amorphous structures can be exploited to minimize undesirable states and ultimately lead to the property improvement.。

四、研究材料與方法

Three types of titanium-related compounds, i.e. ammonium titanyl oxalate (ATO), anatase-TiO2 (ATO) and titanyl tetrachloride (TTC) were employed as precursors for the synthesis of novel titanium oxide compounds. In-situ Raman spectroscopy was used as a major probe to examine molecular details of the coordination and geometry of both amorphous and crystalline species.

五、討論與結論

The thermal decompositions of ATO have been studied by thermogravimetric analysis and Raman spectroscopy. Upon heating, ATO loses water and oxalate molecules and converts to TiO_2 through several stable intermediate whose exact structural and stoichiometric have been determined. On the other hand, hydrolysis of TTC, were conducted under different pH and concentrations in order to generate dominant species with different reactivities which can be manipulated upon reacting with different templates. Evidence is found for the distribution of titanate species are influenced by factors such as pH and temperature, whereas types of precursors do not render significantly impact. In this report, the results here are limited only to the outline of preliminary results; whereas a detailed and extensive report will be published elsewhere.

六、主要參考文獻

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