行政院國家科學委員會補助專題研究計畫成果報告

新型釩氧化物之合成，結構及催化性質之研究

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Abstract

釩氧化物為極重要之製程及環保觸媒。本計畫探討釩氧化物之合成，結構及催化性質。首先，以合成新型之〔V_2O_5/2,2'-bipyridine〕化合物為目標。同時，將其合成及熱分解與〔V_3O_7(1,10-phen)〕比較。然後再對釩氧化物做硫化反應。本計畫對釩氧化物之分子建築及催化科技方面，必能產生具體貢獻及深遠影響。

In this study, the synthetic, structural and catalytic properties of novel [V_2O_5/2,2'-bipyridine] compounds have been conducted. The molecular details of the mechanisms of the thermal decompositions of the novel [V_2O_5/2,2'-bipyridine] compounds have been investigated along with these of [V_3O_7(1,10-phen)]. Sulfation of vanadium oxides have been conducted by impregnation with ammonium sulfate. The result of this study lies in not only synthesis of novel vanadium oxide compounds but also to exercise micro-structural control of synthesis, thermal decomposition and sulfation of vanadium oxides through molecular architecture.

Keywords: Raman, vanadium oxide, catalysis

Scope and Purpose:

Recently, V_2O_5-based catalysts have been utilized in a number of state-of-the-art pollution control technologies. For examples, both the Amoco's DeSOx catalyst and Mobile Oil SOx Treatment (MOST) catalyst consist $V_2O_5/CeO_2/MgAl_2O_5$, and two new NOx/SOx removal techniques, i.e. SNOX (Haldor Topsoe) and DeSONOx (Degussa), also utilized V_2O_5 as their major component.[3-5] Synthesis of novel vanadium oxides: since the discovery of a new class of materials MCM-41 by Mobil's group in 1992, preparation of inorganic materials with novel structures and properties, using structure-directing agents and hydrothermal conditions, have attracted considerable interest owing to their potential applications in catalysis and material science as well as their rich structural chemistry and composition. Recently, a series of reports upon the sulfation of a wide range supported vanadia catalysts have also been reported. [6]The uniform pore diameter of MCM-41 has provided a strategic approach to overcome the limit of microporous materials and open bright future for the molecular architecture of metal oxide-related compounds. The possibility of synthesis of mesoporous and microporous vanadium oxide materials, therefore, might be realized based on a template-assisted route. These hydrothermal methods have widened the scope of the combination between organic and inorganic compounds through hydrogen bonding, van der Waals and hydrophilic-hydrophobic interactions, which cannot be realized by the traditional solid state synthesis Sulfation of Al_2O_3, TiO_2, ZrO_2 and Fe_2O_3, $MgAl_2O_3$, SiO_2, and $MgFe_2O_3$ have attracted much attention due to their roles in Claus process and development of superacid. [28-33] The sulfation of metal oxides (Al_2O_3, TiO_2, ZrO_2 and Fe_2O_3) have been studied mainly by IR spectroscopy due to its unique sensitivity towards the different sulfate structures. Three possible structures of the surface sulfate species have been proposed in the literature.

Results and Discussion

A series of molybdenum oxide/2,2'-bipyridine compounds, such as $[MoO_3(2,2'\text{-bipy})]$, $[Mo_2O_6(2,2'\text{-bipy})]$ and $[Mo_3O_9(2,2'\text{-bipy})_2]$, can be synthesized by the use of MoO_3 as the molybdenum oxide source.[12] In contrast, by the use of WO_3 as tungsten oxide source, a mixture consisting $[WO_3(2,2'\text{-bipy})]$, WO_3 and other unspecified species were formed; whereas monophasic $[WO_3(2,2'\text{-bipy})]$ was obtained by the use of H_2WO_4.[12] Review of the literature concerning metal oxide preparation reveals that the dominant metallate species under hydrothermal condition, which exhibit different reactivities towards templates and consequently play critical roles leading to the formation of final type of metal oxide precursor can be overwhelmingly critical in determining the outcome of the synthesis of these metal oxides. [18-22] However, their detailed mechanisms and correlation are not yet delineated, which greatly hampers the micro-structural to minimize undesirable states leading to the property improvement. The structure of 1,10-phenthanroline and 2,2'-bipyridine are closely related, therefore their coordination chemistry are not expected to differ too much. However, using different vanadium oxide precursors, i.e. V_2O_3 and V_2O_5, products with different coordination between vanadium atoms and the ligands, i.e. $[VO(VO_3)_6(VO(2,2'\text{-bipy})_2)]_2$ [16] and $[V_3O_7(1,10\text{-phen})]$ [12] can be obtained. In comparison, the structures of $[MoO_3(2,2'\text{-bipy})]$ and $[WO_3(2,2'\text{-bipy})]$ have been determined to be isostructural.[1,2,3] They adopt a chain-like framework of corner-sharing distorted octahedral (MO_4N_2) (M=Mo, W) with two terminal M=O bonds, two M-N bonds and two bridging M-O-M bonds.

The role of the metal oxide precursor is believed to affect, both kinetically and thermodynamically, the degrees of oligomerization of various hybrid products. Recently, a series of reports on the sulfation of a wide range supported vanadia catalysts have also been reported.[1,2,3,4] Although the functions of vanadium oxides on sulfuric acide production, de-SOx and de-NOx processes, are well understood, there is a lack of understanding of the structural chemistry between sulfur oxides and vanadia as compared to that of the other metal oxides. Although the sulfation mechanisms of V_2O_5 has been proposed based on the kinetic data, as shown in Figure 4; a direct, spectroscopic evidence for the formation of (V^{+5})-$SO_{2(ads)}$, (V^{+3})-$SO_{3(ads)}$ and (V^{+3})-$SO_{3(ads)}$ has not been provided. [4,5,6]

References

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Expected results and self-evaluation:

The present work will provide not only an impact on the molecular architecture and catalysis technology but also potential commercial utilization.