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学位授与の日付　平成 20 年 3 月 31 日

論　文　名　「Investigations on the Preparation of Ti- and V-based Oxide Catalysts and Their Photocatalytic Reactivities for the Oxidation of Organic Compounds and Elimination of NOx 」(Ti-およびV-酸化物触媒の創製とそれらの有機化合物の酸化反応およびNO_X分解反応における光触媒反応性に関する研究)

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論文要旨

Photocatalysis has attracted a great deal of attention in view of its fundamental science as well as its application to various new technologies. Significantly, it has been applied in the removal of various pollutants and toxic agents in air or water such as in the elimination of NO_x or the complete oxidation of organic compounds into CO_2 and H_2O (degradation). However, in order to develop efficient photocatalysts with high selectivity and reactivity, detailed investigations into the precise control of the local structure as well as local environment of the photocatalytic active sites are vital.

One promising approach in the design of effective and highly active photocatalysts is the use of zeolites since they have well-defined nano-pore structures which provide suitable reaction spaces not only for catalytic but also photocatalytic reactions. The development of photocatalysts encapsulated within zeolite cavities and frameworks as well as MCM-41 mesoporous molecular sieves are of great interest for purification systems which can decompose toxic agents. Microporous zeolites and mesoporous MCM-41 solid porous materials where the framework Si or Al atoms are substituted by various transition metals such as Ti ,V, Mo, Cr, Co, etc. have been investigated and it was observed that highly dispersed Ti-, V-, Mo-, Cr-oxide species exhibit a variety of photocatalytic reactivities with high efficiency and selectivity.

The aim of the present study is the development of zeolites and mesoporous molecular sieves containing highly dispersed various transition metal oxides which are expected to work as photocatalytic active sites. Specifically, the photocatalytic reactivity of transition metal oxides, Ti and V, within the zeolite frameworks has been evaluated for the oxidation of organic compounds as well as the elimination of NO_x. Furthermore, in the practical application of TiO_2 photocatalysts, photoelectrochemical circuit systems consisting of a rod-type TiO_2 electrode and silicon solar cell were constructed and applied for the decomposition of lactic acid in water.

Chapter 1 presents a general introduction of photocatalysis, the physical properties of zeolites and mesoporous molecular sieves materials containing highly dispersed transition metal-oxides as well as their applications for the decomposition of organic compounds or toxic pollutants such as NO_x.

Chapter 2 describes the preparation of TiO_2 within natural zeolite (TiO_2/H-natural zeolite catalyst) and their photocatalytic reactivity for the degradation of 2-propanol. The photocatalytic reactivity of TiO_2/H-natural zeolite catalyst compared with TiO_2 on synthetic zeolites (H-MOR, USY and H-ZSM-5). The TiO_2/zeolites were prepared by an impregnation method and the TiO_2/H-natural zeolite was found to show higher reactivity than the TiO_2/H-MOR catalyst and almost equivalent reactivity to TiO_2/USY. Hydrophobic siliceous zeolites, such as USY (260) and H-ZSM-5 (1880) were found to adsorb larger amounts of 2-propanol than hydrophilic zeolites such as H-natural and H-MOR(15.4). It was also found that TiO_2 fine nano-particles hybridized with a natural zeolite exhibited almost equivalent photocatalytic reactivity for the degradation of 2-propanol in aqueous solution to TiO_2 photocatalysts prepared on synthetic zeolites.

Chapter 3 presents the preparation of TiO_2/ZSM-5 photocatalysts by different methods for the photocatalytic complete oxidation of acetaldehyde with oxygen into CO_2 and H_2O. The effect of the hydrophobicity of the zeolites is first discussed. The adsorption states of H_2O and acetaldehyde molecules on H^+ and Na^+-type ZSM-5 zeolites of different SiO_2/Al_2O_3 ratios were investigated by adsorption isotherm and temperature-programmed desorption measurements. TiO_2 prepared on H-ZSM-5 by an impregnation method showed higher photocatalytic reactivity compared with a standard commercial TiO_2 photocatalyst since the zeolite worked as an effective adsorbent to condense the acetaldehyde molecules. The acetaldehyde molecules interacting with the silanol groups of the hydrophobic H-ZSM-5(1880) could spill over onto the TiO_2 sites, these situations resulting in high photocatalytic reactivity. In contrast, H-ZSM-5(220 and 68) with high Al_2O_3 content were not suitable adsorbents for acetaldehyde, resulting in decreased photocatalytic reactivity. Since the acetaldehyde molecules strongly trapped on the Na^+ sites of the zeolite could not hardly transfer onto the TiO_2 sites, TiO_2/Na-ZSM-5(23.8) showed no photocatalytic reactivity. Moreover, the complete oxidation of acetaldehyde on the TiO_2/ZSM-5 photocatalyst was effectively enhanced by the addition of H_2O vapor. The competitive adsorption of H_2O against acetaldehyde on the TiO_2 photocatalytic sites may depress the highly stabilized acetaldehyde molecules as reactants and/or acetic acid as the intermediate species, resulting in enhanced photocatalytic reactivity by the addition of H_2O vapor.

The enhancement of the photocatalytic reactivity of the TiO_2 nano-particles by simple mechanical blending with hydrophobic ZSM-5 zeolites was also observed. Their photocatalytic reactivity was evaluated for the complete oxidation of gaseous acetaldehyde with O_2 under UV light irradiation. The optimum amount of zeolite powders as an adsorbent for the enhancement of the photocatalytic reactivity of the blended TiO_2/ZSM-5 system was estimated to be ca. 80-95 wt% since the incident UV light was effectively irradiated onto the entire TiO_2 nano-particles due to the high transparency of the siliceous zeolite powders. Furthermore, the hydrophobic zeolite powders efficiently gather the gaseous acetaldehyde molecules within their cavities and supply them onto the TiO_2 surfaces, resulting in an enhancement of the photocatalytic reactivity.

Chapter 4 reports on the preparation of micro or mesoporous materials containing highly dispersed metal-oxide species, such as Ti/USY, V-MCM-41 and imp-V/MCM-41, and their photocatalytic reactivities for the decomposition of N_2O in the presence of CO as well as for the partial oxidation of methane with NO. The Ti/USY catalysts showed photocatalytic reactivity for the decomposition of N_2O into N_2 and CO_2 in the presence of CO at 298 K and exhibited higher photocatalytic reactivity than the standard commercial TiO_2 (P-25) photocatalyst. Various spectroscopic investigations also showed that Ti/USY catalysts with low Ti loadings of 0.5 - 1 wt% involved a highly dispersed Ti-oxide species, while Ti/USY of 5 wt% mainly involved an aggregated Ti-oxide species. Detailed investigations on the relationship between the local structure of the Ti-oxide species and photocatalytic reactivity suggest that the highly dispersed Ti-oxide species acts the active sites for the decomposition of N_2O in the presence of CO.

On the other hand, V-containing MCM-41 catalysts were also prepared by a direct synthesis method under acidic and basic conditions as well as impregnation. Their photocatalytic reactivity was evaluated for the selective photocatalytic oxidation of methane with NO under UV irradiation at 295 K. The selective formation of methanol was observed on V-MCM-41 prepared in acidic solution and imp-V/MCM-41, while only coupling reaction products were obtained on V-MCM-41 prepared in basic solution. The photocatalytic reactivity of the catalysts for the partial oxidation of methane was found to strongly depend on the local structure of the V-oxide species including the coordination and loading sites, i.e., the charge transfer excited states of the isolated tetrahedral V^{5+}-oxide species supported on the catalyst surface acted as the active sites for the selective photocatalytic oxidation of methane into methanol.

Chapter 5 details the construction of photoelectrochemical circuit systems (denoted as TE-SSC-SSE) consisting of a rod-type TiO_2 electrode was connected with rod-type stainless steel electrode through silicon solar cell and their application for the decomposition of lactic acid in water. Light irradiation of this TE-SSC-SSE system led to the efficient complete oxidation of the lactic acid in water into CO_2, suggesting that this system can be practically applied for the clean and safe removal of lactic acid in the human buccal cavity. Furthermore, the negative bias applied on a rod-type TiO_2 electrode by a silicon solar cell was shown to enhance the complete oxidation reaction rate of lactic acid in water.

In Chapter 6, the results and conclusions of these various investigations are summarized and an overview of this thesis is presented.

審査結果の要旨

本論文は、骨格内にTi、Vなどの遷移金属酸化物種を含有するゼオライト触媒を創製し、その上

での有機化合物の酸化反応およびNO_x 分解反応について検討するとともに、遷移金属酸化物種の局所構造と光触媒反応性の関連性を各種分光法により解明することを目的として行った研究をまとめたものである。また、本論分では、TiO_2光触媒の実用化の観点から、棒状TiO_2電極とシリコン太陽電池からなる光電気化学システムを構築し、それを水中の乳酸分解反応に応用する研究も遂行しており、次のような成果を得ている。

(1) 含浸法によりTiO_2を担持した天然ゼオライト（TiO_2/H-natural）がTiO_2/H-MORに比べて 2-プロパノールの酸化分解反応に高い活性を示すことを見いだしている。また、USYのような疎水性ゼオライトは、H-naturalやH-MORのような親水性ゼオライトに比べて 2-プロパノールを効率よく吸着することを明らかにしている。

(2) 含浸法によりTiO_2を担持した H-ZSM-5 (TiO_2/ZSM-5)が、市販のTiO_2と比べてアセトアルデヒドの酸化反応に高い光触媒反応性を示すことを見いだすとともに、これがアセトアルデヒドに対するゼオライトの高い吸着濃縮効果に起因することを明らかにしている。さらに、水蒸気の添加によりアセトアルデヒドの光触媒酸化反応が促進されることを見いだしている。

(3) 含浸法により調製したTi/USY 触媒が、CO存在下においてN_2O をN_2とCO_2に分解する光触媒として作用することを見いだすとともに、USY上に高分散担持されたTi-酸化物種を活性種として本反応が進行することを明らかにしている。また、高分散なV-酸化物種を含有するV-MCM-41 が、メタンをメタノールに部分酸化する光触媒として作用することを見いだしている。

(4) 棒状TiO_2電極とシリコン太陽電池からなる光電気化学システムを用いることで、水中の乳酸を効率的にCO_2まで完全酸化分解できることを見いだすとともに、TiO_2電極に負のバイアスをかけることで反応効率が向上することを明らかにしている。

以上の諸成果は、遷移金属酸化物含有ゼオライト光触媒、およびTiO_2-太陽電池複合システムの創製とその光触媒作用の機構解明に貢献すること大である。また、申請者が自立して研究活動を行うに必要な能力と学識を有することを証したものである。