

STUDY ON THE ROLE OF IRON SPECIES IN PHOTO-RESPONSIVE MONTMORILLONITE COMPOSITES

張, 俐

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氏 名 : 張 俐 (Li ZHANG)

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MONTMORILLONITE COMPOSITES
(光化学応答性をもつ粘土鉱物複合体における鉄成分の役割に関する研究)

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論 文 内 容 の 要 旨

Montmorillonite (Mt) is one of the most representative clay minerals, belonging to 2:1-type clay (smectite group) in which one octahedral Al–O(H) sheet is sandwiched by two tetrahedral Si–O sheets, and well known with its very high cation exchange capacity. Based on the structure and the properties, Mt sometimes plays an important role in environmental remediation of pollutants through adsorption and intercalation in nature. Montmorillonite has been also regarded as an ideal support for photocatalysts because of its great chemical and physical stabilities. In this case it can be possibly developed to the environmental remediation materials by combination with a natural photocatalyst like TiO₂ under solar energy, even though Mt is categorized to an insulator in itself which cannot act as a photocatalyst. Band gap engineering such as heteroatom doping was focused to improve optical properties of insulators and semiconductors by creating middle gap states, resulting in decrease in bandgap energy (E_g). However, heteroatom doping affects sometimes different ways in photocatalysts, that is, sometimes decrease in the crystallinity of the photocatalysts resulting in the decrease in the photocatalytic activity and sometimes generate the new electron trap states leading to increase in photocatalytic activity. Among of transition metal dopants, iron (Fe) is an ideal choice as a doping element because it is a common heavy metal in environments and known to control a number of geochemical cycles in nature. In the present work, the effects of location and localization of Fe^{III} on the photocatalytic mechanism for the composite of Mt with TiO₂ are studied using structural, optical, and electronical characterization techniques to propose the role of Fe species in photo-responsive montmorillonite composites.

In **Chapter 1**, the research background is introduced from both aspects of geochemistry and material sciences. The structures and properties for each component in the composites of titanium oxide (TiO₂) on Mt were described in detail in relation with the photocatalytic reactions. Anatase phase of TiO₂ is well known as a UV-responsive photocatalyst and Mt is one type of clay minerals as well as one of natural 2D materials. Then, the target contaminant models used here were briefly introduced. Hereafter, the objectives of this study were explained.

In **Chapter 2**, the methodologies used in the present work were described for synthesis and characterizations of the TiO₂-Mt composites and the Fe-doping procedures as well as solution analysis.

The potential photocatalytic activity of Mt after Fe^{III} doping was detected via the photocatalytic reduction of chromate (Cr^{VI}O₄²⁻) in **Chapter 3**. Ferric ions (Fe^{III}) -doped Mt prepared by ion-exchange at pH 2 was verified by X-ray diffraction patterns (XRD), Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray absorption near edge structure (XANES). The Fe^{III} doping on Mt at a ratio less than 0.274 mmol-Fe^{III}/g-Mt gained the photocatalytic activity in photocatalytic reduction of Cr^{VI} into Cr^{III} on Fe-Mt, turning into a semiconductor from an insulator. On the other hand, the excess amounts of Fe^{III} doping caused the negative effects probably due to light shielding effect and reduction of active sites for the reaction. The *E_g* of Mt was lowered by generation of a new electron trap state between valence band and conduction band of Mt. This can explain the role of Fe in Fe/Mt as a photocatalyst.

Furthermore, in the composite of Mt with TiO₂, the location of Fe^{III} was investigated from an aspect of photocatalytic activity in **Chapter 4**, that is, whether Fe is located in Mt (Fe-Mt/TiO₂) or in TiO₂ (Mt/Fe-TiO₂). Diffused reflectance spectra (DRS), photo-luminescence spectra (PL), photocurrent (PC), and electrochemical impedance spectroscopy (EIS) measurements revealed that Fe-Mt/TiO₂ composite has greater optical properties, resulting in higher photocatalytic activity in phenol degradation than Mt/Fe-TiO₂ composite. This can be explained by migration of excited electrons from a newly generated electron trap state in Fe-Mt to TiO₂ via Z-scheme heterojunction. Also, the formation of heterojunction could avoid the recombination of photogenerated charge carriers, resulting in enhancement of phenol photocatalytic degradation. Meanwhile, in Mt/Fe-TiO₂, there are no transportation of excited electrons from Mt side via the heterojunction in the composite, resulting in high recombination rate of electron-hole pairs in Fe-TiO₂ side, confirmed by PL.

A replenished study was added to further distinguish the structural Fe^{III} and surface adsorbed Fe^{III} on Mt/TiO₂ composites (*x*Fe-Mt/(1-*x*)Fe-TiO₂ and Fe/Mt/TiO₂) under the same dosage of Fe^{III}. **Chapter 5** compared these two Mt/TiO₂ composites. The photocatalytic activity was greater in the later than the former in phenol degradation, which was also supported by DRS, PL, PC and EIS results. In particular, energy-resolved distribution of electron traps (ERDT) patterns revealed that the amorphous rutile on crystal anatase was the dominant in the later composite (Fe/Mt/TiO₂) which is the most important key component to control the photocatalytic activity, while it was lesser in the former one (*x*Fe-Mt/(1-*x*)Fe-TiO₂). Moreover, existence of Fe^{III} in TiO₂ structure disturbed crystallization of TiO₂ caused the formation of isolated TiO₂ which has less photocatalytic activity.

In **Chapter 6**, environmental implication of the present work was discussed, the conclusions of all chapters were summarized, and the accompanying new challenges were finally proposed.