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論 文 内 容 要 旨

Chapter 1. Introduction

This chapter deals with a brief outline with respect to transition metal oxides as heterogeneous catalysts, and proceeds to the molecular dynamics (MD) simulations and periodic first-principles density functional (DFT) calculations which are two of the most important methodologies towards the study of catalysis, and describes the motivation and objectives of the present study.

Heterogeneous catalysis of transition metal oxides is based mainly on the surface structure of catalyst. It is well known that the heterogeneous catalytic reactions are extremely complicated processes, and it is difficult to reveal the nature of catalysis depending only on the experimental work. A close combination of both experiment and theory can make a breakthrough in catalysis science. Computational chemistry, which is one of the fastest growing areas of chemistry and is used in the present work, provides a very important means to bridge the gap between experiment and theory. The main objectives of this thesis are as follows: (1) to establish reasonable models of vanadium pentoxide (V_2O_5) and titanium dioxide (TiO_2) which are close to the realistic ones; (2) to justify the applicability and effectiveness of the models and methodologies used in the present work; (3) to resolve the essential issues especially concerning the active site present in V_2O_5 surface which have not yet been clarified completely; (4) to reveal and predict new phenomena and new properties of both the oxides in order to contribute to the development of novel TiO_2 and V_2O_5 catalysts with excellent performance.

Chapter 2. Molecular Dynamic Properties of TiO_2 surfaces

In this chapter, the MD simulation was used to investigate the surfaces of the three kinds of TiO_2 phases (rutile, anatase and brookite). It revealed the correlation between the relaxation and coordination regarding the surface atoms: the atoms with small coordination relax much more than the bulk like atoms. The surface atoms undergo vertical as well as lateral relaxations to compensate the missing bonds at the top layer. The driving force

which determines the direction of the relaxation seems to be the improvement of local environments of top layer atoms. It was observed that the (110) surface of rutile is thermally much more stable than the (001) surface; anatase (110) and (001) surfaces exhibit the similar relaxation and stability; for brookite, the (001) surface shows some reconstruction, while the (010) surface is relatively rather stable.

Chapter 3. Molecular Dynamics Simulation of V₂O₅ Surfaces

The bulk structure and three low-index surfaces of V₂O₅ were investigated by using the MD simulation technique. The crystal structure of V₂O₅ was reproduced very well, and the calculated infra-red (IR) absorption bands of V₂O₅ bulk crystal were consistent with the experimental observations. The (010) surface was found to be the most stable, the small energy difference between the (010) surface and bulk corresponds to their geometric similarity. The vanadyl oxygens exposed to the (010) and (001) as well as (100) surfaces were observed to exhibit significant relaxation.

Chapter 4. Geometrical and Electronic Structures of V₂O₅ Bulk and (010) Surface

The DFT calculations on the periodic models were performed to examine the geometrical and electronic properties of both V₂O₅ bulk and (010) surface. The full geometry optimizations of the both were presented. For the bulk, the optimized geometry was found to be very close to the experimental observation, the band gap and binding energy were calculated to be very consistent with the experimental values. From Mulliken population analysis it was observed that the vanadyl oxygens are the least ionic (O^{-0.37}), doubly coordinated oxygens are moderately ionic (O^{-0.56}), while triply coordinated oxygens show the most ionic (O^{-0.68}). The geometrical and electronic properties of the surface were confirmed to be very close to those of the bulk. The weak interlayer interaction was calculated to be 4 kcal/mol. Surface acidic and basic properties were described in terms of projected density of states (DOS) analysis, which suggests the vanadyl oxygen to be more active than di- and tri-coordinated surface oxygens. This methodology rids the restrictions of the cluster approach.

Chapter 5. Reactivity of Lattice Oxygens Present in V₂O₅(010)

One of the key steps in both the selective oxidation of hydrocarbons and SCR reactions is the abstraction of H atom from a reactant by one of the surface oxygens to form surface OH species. Hence, study on adsorption of H atom at V₂O₅ lattice oxygens is necessary for understanding the active sites and reaction mechanisms. Furthermore, it is well known that the interaction between reactant adsorbates and surface is determined not only by the local chemical environment, but also by the contribution of lattice relaxation. To clarify the reactivity of the three kinds of structurally different lattice oxygens of V₂O₅(010) surface, this chapter deals with the adsorption of hydrogen atom by means of the periodic DFT methodology.

The results revealed that the vanadyl oxygen acts as the most active site towards the hydrogen adsorption among the three lattice oxygens. It was confirmed that the lattice relaxation significantly contributes to the reactivity of the oxygens in all the cases, while the local environment of the adsorption site affects both the geometry and reactivity of the adsorption system only in the case of tri-coordinated oxygen. The hydrogen adsorption at these oxygens reduced the surface in different ways. Comparison of the desorption ability of the OH species from the surface showed that removal of the O₁H species, formed by the H adsorption at the vanadyl

oxygen, is energetically preferable. The calculated harmonic vibrational frequencies of the three types of OH species were found to correlate with their corresponding bond strengths and support their respective reactivity. This work indicated that the periodic approach gets rid of the artifacts of the cluster method, and thus the periodic first-principles DFT methodology demonstrates its reliability for investigating the geometric, electronic and catalytic properties of transition metal oxides.

Chapter 6. H₂O Adsorption on V₂O₅(010)

It has been known for many years that the interaction of H₂O with metal oxide surfaces has important consequences for their catalytic behaviors. Taking into account that catalysts are exposed under the ambient conditions, and generally water exists both in reactants and products, the interaction of water molecules with metal oxide surfaces has significant influence on the catalytic behaviors.

The main focus of this chapter involves the investigation of both the molecular and dissociative adsorption of water molecule on the V₂O₅(010) surface using the periodic boundary models and DFT approach. It was observed that the molecular adsorption of water on the V₂O₅(010) surface occurs favorably, whereas the dissociation hardly takes place on the stoichiometric surface due to the significant Coulombic repulsion of the lattice oxygens around the exposed vanadium center to the approaching oxygen of the hydroxyl species. For the molecular adsorption at the surface oxygen sites, it was confirmed that the hydrogen bonding plays a crucial role, and the adsorption abilities of the surface oxygens correlate with the donating ability of electrons from the surface oxygen sites to the adsorbate, and with the ratio of the accumulated charge on the adsorption site and the adsorbed water species. As for molecularly adsorbed water species at the exposed vanadium site, the coordination interaction and hydrogen bonding were found to be the important contribution. For the molecular adsorption, it was elucidated that the vanadyl oxygen plays the most important role among the three surface oxygens and acts as the most favorable adsorption site.

Chapter 7. NH₃ Adsorption on the Brønsted and Lewis Acid Sites of V₂O₅(010)

Many different types of reaction mechanisms have been proposed for the selective catalytic reduction (SCR) of NO by NH₃ over V₂O₅ catalyst in the presence of oxygen. One of the argument towards the SCR mechanisms is the adsorption states of NH₃, which are directly related to the pathway of the reaction. In order to understand the mechanism of the SCR reactions, in this chapter the molecular adsorption of NH₃ on both the Brønsted and Lewis acid sites of V₂O₅ surface are investigated by using the periodic boundary first principles DFT calculations.

The results indicated that ammonia adsorption occurs on both the sites, whereas the adsorption on the Brønsted acid sites was found to be more favorable energetically. Furthermore, the hydroxyl group consisting of the vanadyl oxygen was confirmed to be the most reactive towards the formation of the ammonium species. It was found that ammonia adsorbs on the Lewis acid sites with different coverages, whereas stability under high coverage is low due to the steric repulsion derived from the coadsorbed ammonia molecules. In both the cases, the hydrogen bonding between the N-H and vanadyl oxygen contributes very significantly. For the adsorption on the Brønsted acid sites, the formation of ammonium species was observed which is consistent with the IR observations. Furthermore, it was found that the hydroxyl group consisting of the vanadyl oxygen is the most

reactive site for the formation of ammonium species.

Chapter 8. Mechanism of the Selective Catalytic Reduction of NO with NH₃ over V₂O₅

In this chapter, the periodic first-principles DFT calculations were performed to investigate the active site of V₂O₅(010) surface and the SCR mechanism of NO by NH₃ in the presence of gaseous oxygen. It was confirmed that the NO adsorption on the stoichiometric V₂O₅(010) surface hardly takes place, indicating that the NO cannot form NO₂ molecule with the lattice oxygens of the V₂O₅(010) surface. It gave rationalization in terms of the electronic interactions of the adsorbates with the surface, and concluded that the SCR reaction of NO by NH₃ in the presence of gaseous oxygen follows Eley-Rideal type mechanism which is in agreement with many experimental observations. This study demonstrated again that the periodic first-principles methodology is effective and reliable to investigate the adsorption state and catalytic mechanism with respect to transition metal oxides.

Chapter 9. Summary

The highlights of the present thesis are summarized in this chapter. This study clarified that the vanadyl oxygen of V₂O₅ acts as the active site in catalysis, and the SCR reaction of NO by NH₃ in the presence of gaseous oxygen obeys Eley-Rideal type mechanism. Both the MD simulation and periodic DFT techniques are found to be reliable for investigating the adsorption and catalytic properties of transition metal oxides.

In the present thesis, the established models of V₂O₅ and TiO₂ are proved to be reasonable and reliable for both the MD and DFT studies. At the same time, the applicability and effectiveness of these methodologies are justified, since the various experimental justifications are reproduced very well. On the basis of these periodic models and methodologies, some essential issues especially regarding the active site of V₂O₅ have been elucidated by means of a series of adsorption studies. Furthermore, some new phenomena (e.g. the relaxation behavior of anatase and brookite surfaces) and properties (e.g. the geometrical and electronic properties of the adsorption systems on V₂O₅ surface) have been revealed and predicted for deeply understanding the catalytic nature as well as for designing and developing the novel TiO₂ and V₂O₅ catalysts with excellent performance.

審査結果の要旨

近年、 TiO_2 と V_2O_5 を含む遷移金属酸化物触媒上での炭化水素の選択的酸化反応、アンモニア脱硝反応などにおける触媒活性と選択性の向上が求められている。しかし、その実現には、触媒の活性サイトや反応機構などを原子、電子レベルで解明しなければならない。そこで本論文は、分子動力学シミュレーションと周期的第一原理量子化学計算を活用し、 TiO_2 と V_2O_5 に関するダイナミクス特性、活性サイトおよび脱硝反応機構について検討したものであり、全編9章からなる。

第1章は序論であり、本研究の背景と目的および研究方法について述べている。

第2章では、三種類の TiO_2 結晶 (rutile, anatase, brookite) に分子動力学シミュレーションを適用し、表面微細構造、表面緩和および熱的安定性などを原子レベルで解明している。

第3章では、分子動力学シミュレーションを用い、表面緩和と配位数の関連および表面の熱的安定性を原子レベルで解明している。さらに V_2O_5 結晶に対する IR スペクトルバンドのシミュレーションに成功している。

第4章では、周期的第一原理量子化学計算により得られた V_2O_5 のバルク結晶と (010) 表面の構造や電子状態などが、実験結果と一致することを確認することにより、本計算手法の有効性が検証されている。

第5章では、 V_2O_5 (010) 表面の反応性を調べるため、3種類の格子酸素上への水素原子の吸着状態について検討している。周期的第一原理量子化学計算により得られた結果から、1 配位酸素が酸化反応に対し最も活性が高いことを明らかとし、また、表面緩和や吸着サイトの局所的環境が吸着状態へ与える影響を電子レベルで解明している。

第6章では、周期的第一原理量子化学計算により、 V_2O_5 (010) 表面への水分子の吸着状態を検討し、水分子は表面上に分子状吸着すること、1 配位酸素への吸着が最も安定であること、さらには水分子の解離吸着が起こらないことなどを明らかにしている。

第7章では、アンモニア脱硝反応機構を解明するために、周期的第一原理量子化学計算を用い、 V_2O_5 (010) 表面におけるルイス酸点とブレンステッド酸点へのアンモニア分子の吸着状態について検討している。アンモニア分子はルイス酸点への吸着が弱いのにに対し、ブレンステッド酸点への吸着が強く、特に1 配位酸素を含む水酸基への吸着が最も安定となることを確認している。

第8章では、周期的第一原理量子化学計算を用い、NO 分子が V_2O_5 (010) 表面に吸着しないことを明らかにするとともに、アンモニアによる NO の選択的還元反応が Eley-Rideal 型メカニズムに従うことを明らかにしている。

第9章は本研究の総括である。

以上、要するに本論文は TiO_2 と V_2O_5 の表面のダイナミクス特性、触媒活性サイトおよび脱硝反応メカニズムの検討および予測が、分子動力学シミュレーションと周期的第一原理量子化学計算によって可能であることを実証したものであり、遷移金属酸化物触媒の分子設計、アンモニア脱硝触媒の発展に寄与するところが少なくない。

よって、本論文は博士 (工学) の学位論文として合格と認める。