学 位 論 文 要 旨

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学位論文題目

Establishment of Method for Measuring the Surface Area of Metal Oxides Using Organic Molecule Adsorption and Application on the Development of Supported Metal Oxide Catalysts.
（有機分子吸着による金属酸化物表面積測定法の確立と担持金属酸化物触媒開発への応用）

学位論文の要旨

In the 21st century, sustainable development has emerged as a global imperative. Addressing challenges such as environmental protection, energy security, and industrial upgrading is crucial for advancing human society. As the backbone of the chemical industry, catalysts play a pivotal role in driving cleaner, more efficient technologies. Catalysts enable energy-efficient chemical reactions, reduce waste, and lower emissions, thereby supporting greener industrial processes. They are indispensable in energy applications, such as hydrogen fuel cells and biomass conversion, which aim to reduce dependence on fossil fuels. Similarly, in environmental protection, catalysts contribute to wastewater treatment, air purification, and carbon capture, mitigating pollution and supporting a transition to a circular economy.

Given the importance of catalysts, this work focuses on supported metal oxide catalysts due to their versatility and potential. Traditional methods for measuring surface area, a key determinant of catalytic activity, struggle to evaluate the surface area of metal oxides on support (e.g., TiO_2 on TiO_2/CNT catalysts). To address this limitation, a novel method was developed using the selective adsorption of organic molecules in solution to quantify the surface area of metal oxides on carbon and SiO_2.

Chapter 2 describes the development of a method to evaluate the surface area of various metal oxide catalysts on carbon and silica supports. It was observed that Tiron (TR) and Monosodium 5-Sulfoisophthalate (SS) molecules selectively adsorbed onto metal oxides in DMF solution, while adsorption on carbon and silica supports was minimal. This selectivity was attributed to differences in hydrophilicity, hydrophobicity, and surface acidity or basicity. The selective adsorption of TR and SS was applied to determine the surface area of metal oxides in the subsequent chapters. The adsorption experiments under various conditions, using different molecules and structures, and examined microscopic adsorption models were conducted to understand the adsorption behaviors of TR and SS. Besides developing methods for evaluating the surface area of metal oxide catalysts, these findings can also contribute to the broader understanding of adsorption theory.

Chapter 3 shows a series of examinations of the surface areas of various carbon-supported titanium oxide (TiO_2/carbon) catalysts for hydrogen fuel by using the newly developed TR and SS selective adsorption methods. For N-doped TiO_2 catalysts, a positive correlation was observed between the surface area of titania and catalytic activity when parameters such as trace metal content, annealing time, and oxygen concentration during pyrolysis or annealing were varied. In contrast, Nb-doped TiO_2 exhibited an inverse correlation between surface area and catalytic activity with changes in preparation temperature. This indicates that nitrogen doping significantly improves electrical conductivity, while the effect of niobium doping, which results in lower conductivity, is more dependent on structural changes that influence conductivity and thus catalytic performance. These findings offer important insights into the development of titania-based catalysts for hydrogen fuel cell applications.

Chapter 4 focused on a series of iron oxide catalysts supported by graphene (Fe_2O_3/graphene), prepared by pyrolysis of the precursors of Fe-MOG with graphene supports. These catalysts were characterized using several measurements including XRD, TEM, and TG. The Fe_2O_3/graphene catalysts were applied for the synthesis of imines, and demonstrated high catalytic performance, with yields exceeding 80%. The surface

area of iron oxide on the supported catalysts was determined through the selective adsorption of SS, revealing a positive correlation between Fe_2O_3 surface area and catalytic activity. This work also investigated and estimated the surface area of γ-Fe_2O_3 using XRD analysis, revealing that γ-Fe_2O_3 predominates in these catalysts and is responsible for the catalytic activity. The catalysts were also tested for their versatility and reusability in synthesizing various imines. These findings contribute to advancements in iron oxide catalysts and imine synthesis.

Chapter 5 deals with a series of Fe_2O_3/activated carbon catalysts synthesized via an impregnation method, followed by calcination under an N_2 atmosphere. These catalysts were characterized by various techniques and applied in the direct oxidation of benzene to synthesize phenol using H_2O_2 as the oxidant. The catalytic activity and recyclability were comparable to those reported in the literature. The Fe_2O_3 surface area measured by TR selective adsorption exhibited a slight inverse correlation with catalytic activity, possibly due to inaccessibility of the probe molecules (e.g., TR) into the small micropores of activated carbon. These results contribute to the development of supported iron catalysts and provide valuable insights for advancing the one-step synthesis of phenol from benzene.

In Chapter 6, the focus shifted toward CuO/graphene catalysts. A series of CuO/graphene catalysts were synthesized using an impregnation method, followed by calcination at various temperatures in air. These catalysts were characterized by various techniques and evaluated for their performance in the oxidation of benzyl alcohol to benzaldehyde. The synthesized catalysts demonstrated significantly higher catalytic activity compared to commercial copper oxide powder. A positive correlation between the CuO surface area (measured via selective adsorption of SS) and catalytic activity was observed. Furthermore, the CuO/graphene catalysts exhibited excellent reusability, maintaining activity after simple washing. These findings not only enhance our understanding of copper oxide-based catalytic systems but also provide valuable insights into alcohol oxidation reactions,with potential implications for industrial applications.

This work established a method for measuring the surface area of supported metal oxides through adsorption of probe organic molecules, and applied this method to titanium oxide, iron oxide, and copper oxide catalysts. The positive correlation between catalytic activity and surface area validated the method's effectiveness. This approach could be extended to evaluate the surface area of various carbon and silica-supported metal oxides, aiding in the understanding of surface and catalytic processes for supported metal oxides.

The method developed in this study may also be applicable to other materials like polymers or zeolites. For instance, in alumina-supported gold catalysts, the probe molecule could adsorb on alumina (oxide) instead of gold (metal), allowing the measurement of the support's surface area, with subsequent calculations for the gold surface area. This approach can enable the determination of surface areas in metal oxide/metal catalysts, offering a simpler alternative to the method based on the adsorption of hydrogen or CO.

The development of this specific surface area evaluation method fosters innovative approaches for supported catalysts and has potential applications across various industries. By enhancing the understanding of hydrogen fuel cells, imine synthesis, and alcohol oxidation reactions, this research contributes to advancements in these fields. Furthermore, the adsorption phenomena and the established metal oxide surface area measurement method explored in this study could support applications in other sectors, such as electronic sensors and medical applications, where composite metal oxide materials are essential. Based on these findings and their potential applications, this work aims to contribute to the development of a sustainable society.

Summary

Applicant for degree: Doctor of Engineering

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Title of thesis :

Establishment of Method for Measuring the Surface Area of Metal Oxides Using Organic Molecule Adsorption and Application to the Development of Supported Metal Catalysts

The chemical industry serves as the backbone of modern society, driving productivity and economic development. Catalysts are indispensable in this field, with supported metal and metal oxide catalysts being widely utilized and demonstrating significant potential for various applications. Chemical reactions typically occur on the active surfaces of supported catalysts, necessitating the development of surface characterization techniques. However, existing methods for determining surface area, a critical factor for catalytic performance, are inadequate for accurately assessing the surface area of metal oxides on support. To address this problem and improve the performance of supported catalysts, this research aimed to develop a simple and quantitative method for determining the surface area of metal oxides on supports using organic probe molecules in solution.

First (Chapter 2), the adsorption behavior of organic molecules on titanium oxide was investigated, and their potential as selective probes for metal oxides on supported catalysts was explored. It was revealed that Tiron and Monosodium 5-Sulfoisophthalate in DMF met the criteria for effective probe molecules. These molecules can accurately determine the surface area of metal oxides, such as titanium, iron, and copper oxides, on carbon and/or SiO_2 supports. Their adsorption behavior under various conditions was also examined, providing a detailed analysis of the underlying adsorption mechanisms.

Next, this selective adsorption method was applied to evaluate the surface area of metal oxides in several catalytic systems. These included TiO_2/carbon catalysts for hydrogen fuel cells (Chapter 3), Fe_2O_3/graphene catalysts for imine synthesis (Chapter 4), Fe_2O_3/activated carbon catalysts for benzene oxidation (Chapter 5), and CuO/graphene catalysts for benzyl alcohol oxidation (Chapter 6). Using Tiron or Monosodium 5-Sulfoisophthalate as probe molecules, a clear correlation was observed between the measured surface areas of certain catalytic metal oxides and their catalytic activities. These results validated the reliability of the method developed in this study and provided valuable insights into catalyst design and optimization.

In conclusion, this research successfully developed a method for evaluating the surface area of metal oxides (TiO_x, FeO_x, CuO, ZrO_2) supported on carbon and/or SiO_2, demonstrating its applicability across various catalytic systems. The findings have the potential to advance the field of catalysis by enabling more precise characterization of supported catalysts, ultimately contributing to the development of more efficient and sustainable catalytic processes.