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論 文 題 目	Maximizing Potential of Graphene Oxide for Nanocatalysis
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論文の内容の要旨

Graphene oxide (GO) and its derivatives such as graphene oxide frameworks (GOFs) are widely used as supports in the field of catalysis due to their high specific surface area, and abundance of various functional groupsAlthough properties of GO significantly influence the synthesis of their derivatives and interaction with the supported metal nanoparticles (NPs), the relationship between the properties of GO and the performance of the resultant nanocatalysts has not been systematically studied, which corresponds to the aim of this thesis.

In **Chapter 2**, GOFs have great potential as supports for metal NPs, due to their well-defined and engineerable pores. Since GOFs are prepared by bridging GO sheets with linker molecules, their properties depend on those of GO as the starting material. However, the diversity in the physicochemical properties of GO has prevented understanding key parameters for catalyst design. To address this issue, in this chapter, GOFs and GOF-supported Pd NP catalysts (Pd@GOFs) were synthesized from three GO samples with different properties. They were subjected to systematic characterization and catalytic recyclability test in Suzuki-Miyaura cross-coupling. The major findings are: The density of linker molecules in GOF is crucial for enhancing catalytic recyclability, which is influenced by the abundance of reactive in-plane functional groups in the raw GO samples. The gallery spaces between GO layers are important to maintain uniform dispersion of Pd NPs. GO with too small sheets cannot create such gallery spaces, leading to significant aggregation of NPs. Although GOFs have been demonstrated to be useful for various applications, the importance of the quality of the raw material, GO, has sometimes been overlooked. The results presented in this chapter, which assess the quality of GO samples using a multifaceted method, is valuable for fundamental research and design of nanocatalysts.

In **Chapter 3**, the intellectual design of catalysts is pivotal for developing advanced materials and enhancing various catalytic reactions, including electrochemical water splitting for sustainable energy production. Among different catalysts, Pd on GO supports has shown promise for the hydrogen evolution reaction (HER). Although numerous studies have utilized GO as a support material for HER catalysts, research on which specific properties of GO affect catalytic performance remains relatively scarce. Therefore, in this chapter, various GO materials with different characteristics were selected to synthesize GO-supported Pd NP catalysts. The catalysts were evaluated in HER. The properties of the GO materials were characterized using multiple techniques, and their catalytic performance was evaluated through linear sweep voltammetry (LSV) and electrochemical surface area normalization. The LSV results are shown in Figure 2. Firstly, the Pd NP catalyst supported on GOFs did not exhibit promising performance (not shown), but those of GOs showed reasonable performance, which is apparently an opposite trend compared to the Suzuki-Miyaura reaction discussed in Chapter 2, suggesting the importance of diffusion resistance in HER. Among all the catalysts, Pd/GO-GNP (GO prepared from graphene nanoplates (GNP)) exhibited the best HER performance, with the largest electrochemically active

In **Chapter 4**, GOFs using several different linkers with varying functional groups were synthesized, aiming to investigate their effects on the structural and catalytic performance of GOF-confined catalysts. FTIR and XRD analyses revealed that linker types and amounts influence GOF properties, such as interlayer spacing and functional group retention. Pd@GOF catalysts, synthesized by incorporating palladium NPs into GOFs, were tested for their performance in the Suzuki-Miyaura coupling reaction. Catalytic tests demonstrated that the linker's functional groups significantly affect activity and durability, highlighting the importance of balanced functional group availability and sufficient pillar density for retaining Pd NPs. Comparisons between GOF-confined and GO-supported catalysts indicated that GOFs effectively prevent NP agglomeration while offering enhanced recyclability. The study also noted that commercially sourced GO, with fewer in-plane functional groups, impacted catalytic retention. These findings provide valuable insights into designing high-performance GOF-based nanocatalysts by optimizing linkers and GO surface functionalization to meet diverse catalytic requirements.

In conclusion, this thesis highlights the pivotal role of GO's physicochemical properties and linker design in optimizing nanocatalyst performance. By systematically exploring the relationship between GO characteristics, linker functionality, and catalytic behavior, the findings offer a comprehensive understanding of material design strategies. This work provides a foundation for developing high-performance GOF-based catalysts tailored for specific reactions, bridging fundamental research and practical applications in sustainable catalysis and energy production.

Keywords: Graphene oxide; Nanocatalysts; Graphene oxide framework, Suzuki-Miyaura coupling reaction,

論文審査の結果の要旨

本論文は、酸化グラフェン（GO）の化学的・物理的な構造を様々な分析法によって明らかにし、鈴木-宮浦カップリング反応や水素発生反応（HER）を例に、ナノ触媒担体として活用する上での設計則を明らかにしたものである。

ナノ触媒は高い活性や特異な反応性といった点で優れるが、活性種の高分散を維持するために高度な担体設計を必要とする。GO は高い表面積、柔軟かつ優れた物理的安定性、容易な修飾性を有し、ナノ触媒の担体として幅広い応用が期待されている。一方、GO、またはその誘導体を担体とした触媒の性能や性質は、大本の原料である GO の性質に大いに影響されると考えられるが、既存の研究の多くはアプリケーションや誘導体そのものの新規性に注視しがちで、GO の品質や性質については、その重要性にも関わらず、見過ごされがちであった。本研究は GO のナノ触媒担体としての可能性を拡大すべく、ナノ触媒担体としての GO とその誘導体の構造と性能の関係を明らかにすることを目指した。

第 2 章では、異なる原料から様々な特性を持つ GO を合成し、リンカーを通して GO シートを接合した酸化グラフェンフレームワーク（GOF）へ誘導し、鈴木一宮浦カップリング反応用の Pd ナノ粒子触媒の担体とした。XRD、TG-DTA、XPS などの分析を通じて、触媒のリサイクル性は面内官能基の量と種類（GOF のリンカー密度の向上につながる）に依存し、ナノ粒子の均一分散には GO 層の横方向の寸法が必要であることを明らかにした。

第 3 章では、HER における GO 担持 Pd ナノ粒子触媒の性能を比較し、GO の物理化学的特性が電気

触媒性能に与える影響を調査した。面外官能基による Pd の安定化と面内官能基の低減を両立した設計が鍵であり、小サイズの GO シートが効率的な電子輸送ネットワークの形成に有効であることがわかった。

第 4 章では、異なる官能基を持つリンカーを用いた GOF を合成し、リンカーの官能基の量と種類が触媒性能に与える影響を検討した。GO 表面の反応性官能基の残留量とリンカーの性状（結合の安定性）が、ナノ粒子の固定化と溶出防止に重要であることが示された。

本研究では、GO の特性がカップリング反応や電気化学反応に用いられるナノ触媒の担体としての機能に及ぼす影響を明らかにした。これにより、高性能ナノ触媒の設計における GO の重要性が浮き彫りになり、高品質な GO ベースのナノ触媒の合成に役立つ知見が多く得られた。GO とその誘導体を用いたナノ触媒は今後益々利用が拡大することが見込まれており、関連分野への貢献は極めて大きい。よって、博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。