

N-ヒドロキシフタルイミドおよび担持 Pd 触媒を用いたアミドの α 酸素化反応

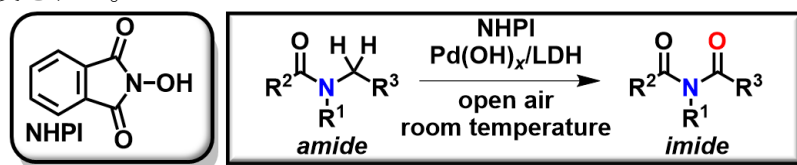
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Aerobic α -Oxygenation of Amides Using *N*-Hydroxyphthalimide and Supported Palladium Catalysts (¹*School of Engineering, The University of Tokyo*) ○Nobuki Hachimura,¹ Takafumi Yatabe,¹ Daisuke Takei,¹ Kazuya Yamaguchi¹

Amides and imides are present ubiquitously in many natural compounds, industrial products, and pharmaceuticals. Imide synthesis via α -oxygenation of amides without changing their original skeletons is a useful molecular transformation. However, such oxygenation reactions are difficult due to the electron deficiency of the α -carbon of amides, and there are few reports on the amide oxygenation using molecular oxygen as the terminal oxidant.¹ In this study, we have successfully developed an α -oxygenation reaction of amides to imides at room temperature in the presence of *N*-hydroxyphthalimide and Mg₃Al-CO₃ layered double hydroxide-supported Pd hydroxide (Pd(OH)_x/LDH) catalysts using O₂ in the air as the sole oxidant. This oxygenation reaction system can be applied to a variety of secondary and tertiary amides. When the Pd(OH)_x/LDH catalyst was removed by filtration during the reaction, the reaction immediately stopped, and Pd species were not detected in the filtrate by ICP-AES analysis. Moreover, the reaction hardly proceeded when homogeneous Pd catalysts were used. These facts suggest that the reaction proceeds on the surface of Pd(OH)_x/LDH.

Keywords : *Supported Pd Catalyst; N-Hydroxyphthalimide; Amide Transformation; Imide Synthesis, Aerobic Oxidation*

アミドやイミドは多くの天然物や工業製品、医薬品に遍在しており、アミドの骨格を維持した α 酸素化反応によるイミド合成は有用な分子変換である。しかし、このような酸素化反応はアミドの α 炭素が電子不足であることから困難であり、分子状酸素を酸化剤とした報告はほとんどない¹⁾。本研究では、*N*-ヒドロキシフタルイミド (NHPI) および Mg₃Al-CO₃ layered double hydroxide (LDH) 担持 Pd 水酸化物触媒 (Pd(OH)_x/LDH) によって、室温で空气中酸素を酸化剤としたアミドの α 酸素化反応の開発に成功した。本反応系は様々な第 2 級、第 3 級アミドの α 酸素化に活性を示した。また、反応途中で固体触媒をろ過により取り除いたところ反応が直ちに停止し、ろ液の ICP-AES 分析で Pd が検出されず、均一系 Pd 触媒ではほとんど反応が進行しなかったことから、本触媒系は不均一系触媒として機能し表面上で反応が進行していることが示唆された。



- 1) The Oxidation of Amides to Imides: A Powerful Synthetic Transformation. J. Sperry, *Synthesis* **2011**, 3569–3580.