Ni-Zn 複塩基性塩触媒の高分散担持法の開発とエポキシ化反応への応用

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Development of Highly-dispersed Ni-Zn Hydroxy Double Salt Catalyst and Its application for Epoxidation of Enones With Hydrogen Peroxide

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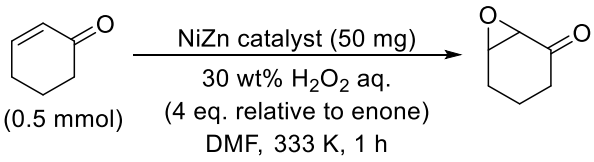
We have designed highly functional nanostructure catalysts by using the anion-exchange ability of acetate-intercalated Ni-Zn hydroxy double salt (AcO^-/NiZn), and applied them to various liquid-phase organic transformations [1)]. For the improvement of their catalytic activity as a Brønsted base in this work, highly dispersed NiZn onto SiO_2 surface is synthesized by the addition of SiO_2 as a support during hydrothermal preparation.

In the XRD profiles of synthesized catalysts (AcO^-/NiZn_SiO_2), the peaks based on the AcO^-/NiZn was observed. Moreover, the small and dispersed particles were immobilized on the surface of support, confirmed by SEM images. Additionally, in the case of the epoxidation reaction of 2-cyclohexen-1-one with H_2O_2, the AcO^-/NiZn_SiO_2 catalyst showed higher catalytic activity than that of AcO^-/NiZn, based on the normalized value between epoxy ketone and the amount of Ni^{2+} and Zn^{2+} in the catalyst matrix.

Keywords ; Ni-Zn Hydroxy Double Salt; Solid Base Catalyst; Epoxidation; Hydrogen Peroxide

当研究室では、アニオン交換性層状 Ni-Zn 複塩基性塩 (NiZn)のアニオン交換能を駆使して高機能なナノ構造触媒を設計し、様々な液相有機合成反応に応用してきた [1)]。本研究では、酢酸アニオン導入型 NiZn (AcO^-/NiZn)を水熱合成する際、支持体としてシリカを共存させることでシリカ表面に微細な NiZn を高分散担持させた触媒, AcO^-/NiZn_SiO_2, を合成し、触媒活性を向上させることを目指した。

合成した AcO^-/NiZn_SiO_2 触媒の XRD には、AcO^-/NiZn の層状構造に特有の回折ピークが確認され、SEM 像からはシリカ担体表面に微細な AcO^-/NiZn が集積していることがわかった。また、2-cyclohexen-1-one のエポキシ化反応を行った際、エポキシケトンの生成量を触媒に含まれる Ni^{2+}と Zn^{2+}カチオンの和で規格化した値を算出したところ、AcO^-/NiZn_SiO_2 触媒の方が大きくなり、高い触媒活性を示すことがわかった。



catalyst	epoxy ketone (mmol) /total Ni^{2+} + Zn^{2+} (mmol)
AcO^-/NiZn	0.66
AcO^-/NiZn_SiO_2	**0.80**

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