固体酸触媒を用いる脱水的連続フローアミド化反応

（東大院理[1]・東大院 GSC 社会連携講座[2]）石谷暖郎[2]・○武野晃太[1]・笹谷将洋[1]・小林修[1,2]

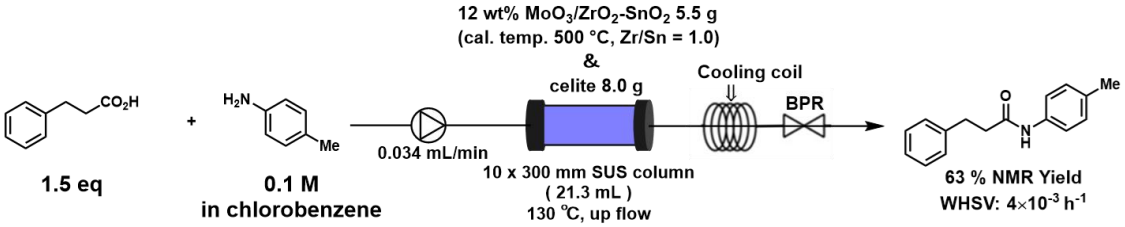
Development of Direct Dehydrative Amide Formation with Solid Acid Catalysts under Continuous-flow Conditions

(GSC Social Cooperation Laboratory[1] and School of Science,[2] The Univ. of Tokyo)
Haruro ISHITANI,[1] ○Kota TAKENO,[2] Masahiro SASAYA,[2] Shū KOBAYASHI[1,2]

Synthesis of amides from carboxylic acids and amines is one of the most widespread processes for manufacturing value-added chemicals. The syntheses have been highly relied on stoichiometric activation using coupling reagents, and thus catalytic amidation supplying atom economic and greener methods is strongly demanded.[1,2] A continuous-flow system with a catalyst-packed reactor additionally has a great deal of potential to address issues of efficiency in synthesis and in controlling productivity. To access this purpose, we started an investigation by choosing suitable solid acids for the direct condensation under batch conditions. After screening typical solid acids, we found that the reaction was significantly enhanced by using molybdenum oxide supported on a mixed metal oxide composite. A careful investigation on the effect of supports indicated that Zr/Sn mixed oxide gave the highest catalytic activity among tested. We transferred the given conditions into a continuous-flow system, and carefully explored relationships between WHSV and outcomes under various reaction conditions.

Keywords: Solid Acid, Molybdenum Catalyst, Mixed Metal Oxide Composite, Catalytic Amidation, Continuous-flow Reaction.

カルボン酸とアミンによるアミド化は、化成品合成全般に広く利用されているが、化学量論量のカップリング剤や活性化試薬を用いない触媒を用いる直接的な合成も汎用品の製造においては重要である。[1,2] また連続フローへの展開により、高効率と高生産性が期待できる。本研究で演者らは、固体酸触媒による脂肪族カルボン酸とアニリン類の直接的フローアミド化反応を検討した。バッチ法による予備検討では、代表的な固体酸触媒のうち酸化モリブデン担持複合金属酸化物が高い活性を示した。中でも Zr/Sn 複合金属酸化物担体を用いた場合、ほぼ定量的に目的のアミドを与えた。これを基準とし、連続フロー条件下において重量空間速度と収率の関係、反応温度、滞留時間の効果を詳細に検討した。カルボン酸を 1.5 等量、カラム温度を 130 ℃とした連続フロー条件下では、WHSV = 4x10^{-3} h^{-1} のとき 63%収率で目的のアミド化合物を得ることができた。



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