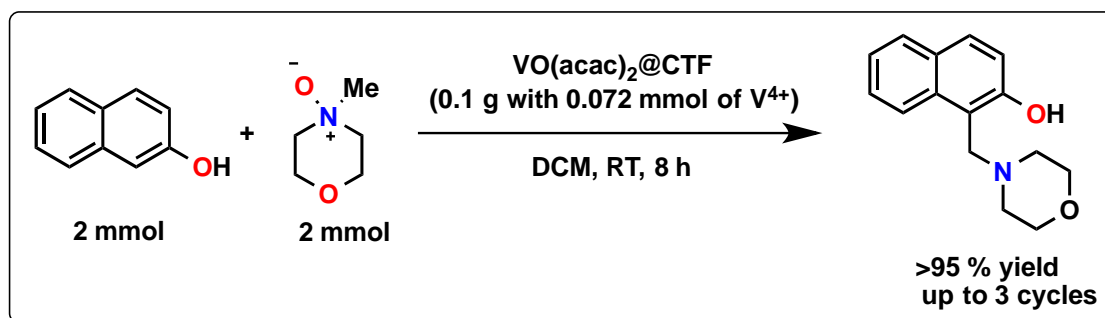


Catalysis by Design: A Modified Mannich Type Reaction Catalyzed by VO(acac)₂ Supported on Covalent Triazine Framework

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Engineering porous materials such as Metal Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) with active homogenous catalytic sites would offer new opportunities in the field of heterogeneous catalysis. Among COFs, Covalent Triazine Frameworks (CTFs) are high performance polymer materials with intrinsic repetitive triazine moieties, high surface area and regular porosity. In general, these materials are synthesized from respective nitrile monomers via either ionothermal route or by CF₃SO₃H catalyzed trimerization reactions. Therefore, designing new nitrile based linkers with active binding sites (N⁺N, N⁺O, O⁺O, etc) and syntheses of corresponding new CTFs may offer new challenges in designing efficient heterogeneous supports for more sustainable and environment-friendly society. In this regard, novel acetylacetone based CTFs were synthesized using 4,4'-malonyldibenzonitrile under ionothermal conditions ^[1] using ZnCl₂ at different temperatures and at different molar ratios of linker and ZnCl₂. The resulting CTFs showed high specific surface areas (1500-2600 m²/g) and high stability (>400 °C). The incorporation of highly polar acetylacetone group enhanced the interaction with CO₂ and H₂ and the CTFs showed CO₂ uptake up to 3.16 mmol/g at 1 bar and 273 K and H₂ uptake up to 1.5 wt% at 1 bar and 77 K. Additionally, VO(acac)₂ was incorporated on the resulting CTF by post-synthetic modification and the resulting VO(acac)₂@CTF showed excellent reactivity for modified Mannich-type reactions ^[2]. The designed VO(acac)₂@CTF showed higher catalytic reactivity than the homogenous catalyst with wide substrate scope and reusability. The turn over number obtained from the designed heterogeneous catalysts is three times more than the homogenous catalyst and can be reused for minimum of five repeated cycle of reactions.



Scheme 1. Schematic representation of modified Mannich type reaction catalyzed by VO(acac)₂ supported on Covalent Triazine Framework

References

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